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CONTRIBUTION TO THE BIOCHEMISTRY OF SEWAGE PURIFICATION; THE BACTERIOLYSIS OF PEPTONES AND NITRATES.[1]

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CONTENTS.

Introduction.—Statement of the problem; Methods of investigation; Methods of chemical analysis; Source of the cultures.

Review of the Literature.—Putrefaction and decay; Ammonification; Nitrification; Nitrogen liberation; Fixation of atmospheric nitrogen; Denitrification; Liberation of nitrogen from nitrated solutions.

Discussion of Experimental Data.—Ammonification; Denitrification; Nitrite formation; Reduction of nitrates to ammonia; Undetermined nitrogen from nitrates; Gain and loss of nitrogen; Distribution of ammonifying and denitrifying bacteria in sewage and sewage effluents; Relation of peptonization to the other biochemical functions.

Conclusions.

[1] Read at the 31st general meeting of the American Chemical Society, Philadelphia, Pa., December 28, 1904. The studies here reported were made at the Lawrence Experiment Station, under the direction and with the cooperation of Mr. H. W. Clark. In the chemical analyses the writer has been assisted by Mr. Geo. O. Adams, who has also aided in the elaboration of the methods and in the discussion of the significance of the results. In reviewing the literature, free use has been made of the various publications of Doctors Rideal, Chester and Lipman, and in many instances, where the original articles could not be obtained, citations have been made from the reviews of these authors. Published also in the *Tech. Quarterly*, March, 1905.

INTRODUCTION.

In the biological treatment of sewage a large number of complex chemical reactions occur, and many types of bacteria are active, some of them playing a good part in the purification, while others exert a hindering action. Hitherto, the analyst has relied on chemical methods in order to judge of the degree of purification accomplished by a given sewage system, and, indeed, as far as they go, the chemical methods have been sufficient for that purpose. In the use of the so-called biological sewage disposal systems, however, with their more scientific control, it has been found that the chemical methods of the present time are inadequate, inasmuch as they do not show what processes are active within the filtration plant further than can be shown by the end products, that is, they do not show in what manner those end products are produced, nor do they indicate in what manner the intermediate processes may be controlled in order to accomplish the greatest amount of purification in the most economical manner. While much knowledge of the methods of filter control has been acquired, this knowledge has been acquired by the cut and try method, rather than by the study of the processes going on in the filters and of the different types of bacteria which are responsible for the various types of reaction.

It has often been noticed that while one method will dispose of a certain sewage in a satisfactory manner, a very different result is obtained when we attempt to treat a different sewage by this process, and this has led to the axiom, that the problem of finding a satisfactory disposal method is an individual one for each sewage. The reason for this is twofold—first, the very great variation in the character and amount of the components of the sewage, and, second, the difference in the active bacterial flora of that sewage.

During the past few years, much study has been given to the bacteriology of sewage at the Lawrence Experiment Station, and recently new methods have been devised for the study of the functions of the bacteria concerned in the purification of sewage, and these methods, with some of the results obtained by their use, have already been published.[1] In the treatment of sewage, the main problem is to accomplish the change of the nitrogenous matter from the organic to the inorganic form, since in the process

[1] Clarke and Gage: *Eng. News*, **53**, 27 (1905).

of changing the form of the nitrogen, the carbonaceous matter, except, perhaps, a very small portion, is usually taken care of. Thus a knowledge of the bacterial flora of sewage and of the changes which different types of bacteria may cause in the form of the nitrogen of that sewage becomes of considerable importance in the proper control of those changes. The greatest difficulty in investigations of this character is the uncertainty of the organisms in the sewage. The least change in the conditions of the experiment, and new species of bacteria develop, with perhaps a total change in the character of the chemical reactions produced, thus assuming that the experiment is conducted under conditions similar to those under which sewage disposal systems are operated. In order to understand the fundamental principles of sewage purification it becomes necessary to study the functions of the various species of bacteria in pure culture, and under conditions which can be controlled, for it is only by such methods that data sufficiently exact to be used in an analysis of the more complex problems where mixed cultures of bacteria are active and the products of their activity react upon one another, may be obtained. The present paper has to deal with the changes caused in the nitrogen content of known solutions by pure cultures of bacteria.

METHODS OF INVESTIGATION.

The method employed in this experiment has been to inoculate two solutions, one containing nitrogen in the form of peptone and the other containing peptone and nitrogen in the form of potassium nitrate, with pure cultures of bacteria, and to determine accurately from day to day the changes taking place in the nitrogen content of the solution as far as could be judged by making quantitative tests of the amount of nitrogen present in the solutions as ammonia, as nitrates, and as nitrites, and by determining at the end of a stated period the total amount of organic nitrogen in the solutions by the Kjeldahl method.

The peptone solutions have been uniformly composed of 0.1 per cent. of Witte's peptone in distilled water, with an organic nitrogen value of about fourteen parts of nitrogen per 100,000 as determined by the Kjeldahl method. It is well known that commercial peptones are not pure and that they contain considerable amounts of albumoses and of other hydrolyzed albumens. This fact, however, is an advantage rather than a detriment in a study

such as the present, since the cultural solutions simulate more closely the character of sewage and are at the same time of sufficiently definite composition to allow of their being readily duplicated in the laboratory.

The nitrated solutions have been made up the same as the peptone solutions, with 0.1 per cent. of Witte's peptone in distilled water and have been of three different strengths at different periods of the investigation, containing nitrogen as potassium nitrate equivalent to 2.7, 6.0 and 22.5 parts per 100,000.

The cultures selected were first purified by plating out on gelatin and were then subjected to a thorough course of revivification by successive cultivations in broth, after which they were transferred to agar streaks. Glass-stoppered bottles, containing about 100 cc. of the peptone solution and of the nitrated peptone solution, were then inoculated with a large loop full of the culture from the surface of the agar streaks, and after thoroughly shaking, the bottle cultures were incubated at 20° C. Portions for analysis were removed from each bottle daily with sterile pipettes, each culture being thoroughly shaken before the sample was removed. At the end of the experiment, determinations were made of the total organic nitrogen in both cultures and uninoculated solutions.

By the use of a peptone solution of known strength both with and without nitrates, we have been able to determine approximately, (1) the amount of ammonia formed from the organic matter, that is, from the peptone; (2) the amount of ammonia formed from organic matter plus that formed by reduction of nitrates to nitrites; (3) by subtracting the amount of ammonia formed from the peptone from that formed in the nitrated peptone solution, we obtain a value for the ammonia formed from the nitrates, although there is a large error in the use of this value as will be shown further on; (4) we also obtain a value for the amount of nitrates destroyed by the culture by subtracting the amount of nitrate in the solution from that at the start; (5) we get the amount of nitrites by direct reading; (6) by subtracting the sum of the nitrites and the estimated amount of ammonia formed from the nitrates from the total amount of nitrate reduced, we obtain a value for nitrogen from nitrates unaccounted for, which may have been liberated as free nitrogen. In obtaining this last value we have the sum of all the errors of the other determinations, so that the

value is itself subject to much doubt, but some of the results have been so characteristic that they are used further on with no further apology; (7) by the use of the Kjeldahl values, in connection with the nitrate, nitrite and ammonia values, we are able to compute, with more or less accuracy, the gain or loss in the total nitrogen content of the test solutions. In addition to the study of the cultures mentioned, examinations have been made of a large number of cultures at the end of a seven-day incubation, and certain of these results are included here.

All of the methods, both chemical and bacteriological, have been subjected to more or less unavoidable error. It should be borne in mind, however, that biological processes are always subject to a large variation, and that all results of biochemical investigation should be interpreted in that light. It has, accordingly, been considered sufficiently accurate to determine the various chemical factors to the nearest 0.1 part in 100,000, and to use the results so obtained, for the purposes of discussion as though the errors had been eliminated.

METHODS OF CHEMICAL ANALYSIS.

The methods for the quantitative determination of ammonia, nitrates and nitrites, in these solutions have varied somewhat from the usual procedure for water analysis. For the ammonia determination one cubic centimeter of the solution was placed in the nessler tube, made up to 50 cc. with ammonia-free water, and nesslerized, direct readings being made against permanent standards.

The direct reading of the ammonia is preferable to the distillation method, as the partially decomposed bacterial products do not show as free ammonia in the direct reading, but many of them are broken down by heat and appear as free ammonia by the distillation process, giving ammonia values which are too high. The main objection to the direct reading is the green color which appears in many cultures upon nesslerizing, probably caused by the presence of amines. The green color interferes very much with the matching of the colors against the usual ammonia standards, and it was necessary to use a special set of standards in order to get comparable readings. These standards are a modification of Jackson's platinum cobalt standards[1] in which the yellow is

[1] Jackson: *Tech. Quarterly*, **13**, 314 (1900).

toned down by the addition of cupric chloride solution. There is considerable variation in the shade of different cultures of bacteria after nesslerization, and many experimental sets of standards were made up before the proportion of copper solution was finally decided upon. Since some of the cultures did not produce the objectionable green shade, it was found advisable to keep on hand two sets of standards, one with and one without the copper. The final composition of the special standards employed is shown in the following table.

TABLE I.—PERMANENT STANDARDS—NITROGEN AS AMMONIA—USED IN DETERMINING AMMONIFYING POWER.

Standard. Cc.	Platinum solution. Cc.	Cobalt solution. Cc.	Copper solution. Cc.
0.1	1.8	0.0	0.6
0.3	3.2	0.0	1.3
0.5	4.5	0.1	1.8
0.7	5.9	0.2	1.8
1.0	7.7	0.5	1.5
1.3	9.4	0.9	1.5
1.7	11.5	1.7	2.0
2.0	12.7	2.2	2.0
2.5	15.0	3.3	0.5
3.0	17.3	4.5	0.0
3.5	19.0	5.7	0.0
4.0	19.7	7.1	0.0
4.5	19.9	8.7	0.0
5.0	20.0	10.4	0.0

Platinum solution=2 grams potassium platinic chloride dissolved in a small amount of water. 100 cc. of strong hydrochloric acid (sp. gr. 1.20) added, and made up to one liter.

Cobalt solution=12 grams cobaltous chloride dissolved in a small amount of water. 100 cc. of strong hydrochloric acid added and made up to one liter.

Copper solution=12 grams dry cupric chloride dissolved in water. 100 cc. strong hydrochloric acid added and made up to one liter.

To determine the nitrites, one cubic centimeter of the solution was mixed with 49 cc. of nitrate-free water in the nessler tube and read by the usual Greiss method. The nitrates were determined by placing one cubic centimeter of the culture in round-bottomed tubes having a length of about 70 mm., and a diameter of 15 mm. These tubes were placed in wire racks and the contents evaporated to dryness on the water-bath, or better, in the hot-

air-bath at a temperature of 115° to 125° C. Phenoldisulphonic acid was then added directly to the tube and by rolling the tube in the fingers, was thoroughly incorporated with the residue. The contents of the tubes were then washed into nessler tubes, ammonia was added, the contents made up to 50 cc., and the amount of nitrogen as nitrates read against standards as usual. The evaporation in tubes is preferable to the usual evaporation in dishes, both for economy of space and ease in manipulation. Experiments showed that the evaporation to complete dryness at these temperatures did not affect the accuracy of the determinations.

SOURCE OF THE CULTURES.

The cultures selected were obtained from sewage and from the effluents of sewage filters during a study of the functions of the various kinds of bacteria concerned in sewage purification, and were selected as producing as many as possible of the various changes in the nitrogen content of the test solutions. In all, some forty cultures were studied in detail, and from the results obtained, twenty cultures have been selected as giving results sufficiently characteristic to warrant their being included here. The majority of the cultures not included, gave results which showed nothing further than could be shown by the cultures presented, while others of the cultures omitted had breaks in the chain of results due to losses during chemical analysis. The cultures were isolated during February and March, 1904, as follows:

Cultures 1, 16, 17, 23, 40, 41, from Lawrence sewage.

Culture 18, from septic sewage.

Cultures 4, 7, 9, 10, 11, 13, 29, from the effluents of intermittent sand filters receiving Lawrence sewage.

Culture 22, from the effluent of a contact filter receiving Lawrence sewage.

Cultures 31 and 32, from the effluent of a contact filter receiving septic sewage.

Cultures 24, 26, 38, from the effluents of intermittent-continuous filters receiving Lawrence sewage.

It is not essential in a study of this kind that the names of the species be known. Indeed, in sewage disposal, a determination of the presence or absence of definite species of bacteria, other than certain disease-producing organisms, is of small

moment compared with the establishment and determination of the types which play important parts in the conversion of that sewage into a harmless and inoffensive water. While some progress has been made in the study of these cultures, the complete species tests are not complete at the present writing. Enough work has been done, however, in order to be able to say that the cultures are apparently all different species, and indeed, the variation in the nitrogen changes caused by these cultures would alone be almost sufficient to establish this difference.

REVIEW OF THE LITERATURE.

We will now discuss the changes which may occur in nitrogenous matter and the agency of bacteria in causing those changes. As sources of nitrogen in the experimental solutions, we have peptone and atmospheric nitrogen common to both solutions. In the peptone solution the only changes which may be produced by bacterial action are the breaking-down of the peptone into amides and amino-acids, which themselves may then be broken down with the formation of ammonia or free nitrogen, the oxidation of the ammonia to nitrates and nitrites, and the fixation of atmospheric nitrogen. The process going on here is primarily putrefactions or decay, the term putrefaction being used in the sense of breaking down without air or anaerobic action, the term decay being used as indicating an oxidizing or aerobic action.

Owing to the newness of bacteriological methods of sewage disposal we have to turn mainly to the agricultural chemists and bacteriologists for our knowledge of the biochemical processes by which nitrogen is changed from one form to another. As early as 1837, Schultze[1] and Schwann[2] discovered that the cause of putrefaction and decay was always present in unsterilized air, but it was left to Pasteur[3] and his co-laborers to demonstrate that putrefaction was due to the action of micro-organisms. The first step which takes place in the conversion of the albuminous matter in sewage is peptonization or liquefaction of the insoluble proteids into soluble peptones and albumoses. The consideration of this step may be omitted here since we are starting with these latter products. The next step in the process is the conversion of peptones into amino acids and amines.

[1] Schultze: *Pogg. Ann.*, **39**, 487.
[2] Schwann: *Ibid.*, **41**, 184.
[3] Pasteur: *Compt. Rend.*, **48** (1859); **50**, 849 (1860).

The amino acids are next decomposed into organic acids and free nitrogen or ammonia, the organic acids and the ammonia thus formed combining to form ammonium salts, but these salts are rapidly broken up and converted into carbon dioxide, water, ammonia, hydrogen, nitrogen and marsh gas, the last three of which escape with some of the ammonia and carbon dioxide, leaving the rest of the ammonia and carbon dioxide united with the mineral elements in the solution or combined as ammonium carbonate.

Ammonification.—There is much experimental evidence to show that the production of ammonia from organic matter is characteristic of most species of bacteria. Marchal[1] found that out of thirty-one organisms studied, seventeen produced ammonia decidedly, and all of the others gave a slight reaction. He observed that the conversion of organic matter into ammonia is inversely proportional to the amount of organic matter in solution, and varies with the character of the proteid matter, the breaking-down of peptones being more rapid than that of most other albuminous compounds. Sewerin[2] found that the majority of bacteria which he studied produced ammonia, but the rate of ammonification was very variable, some of the species producing ammonia continuously from the start, while others did not show any reaction until after some days. Chester[3] found that the majority of common soil bacteria were able to produce ammonia, and also that the rate of ammonification in a soil which had been manured was directly proportional to the product of the numbers of bacteria in that soil, and of their relative ability to produce ammonia.

The increase in ammonia in sewage on standing, and the conversion of organic nitrogen to ammonia in septic tanks and in contact filters are common knowledge in sewage analysis.

The ammoniacal fermentation of urea, while not directly applicable to the present experiments, has considerable significance in sewage treatment. This subject has been thoroughly studied by Pasteur,[4] Gabler,[5] Felz and Riter,[6] von Jaksch,[7] Miquel,[8] Leube,[9]

[1] Marchal: *Arc. Science*, **8**, 574 (1894).
[2] Sewerin: *Cent. f. Bakt.*, i (2), 167 (1895).
[3] Chester: Bull. 65, Dela. Agr. Expt. Sta., 1904, p. 69.
[4] Pasteur: *Compt. Rend.*, **49**, 1 (1860); *Ann Chem. and Physiol.*, **64** (1862).
[5] Gabler: *Compt. Rend.*, **64** (1874).
[6] Felz and Riter: *Jour. de l'Anat. and Physiol.*, 1874.
[7] von Jaksch: *Zeit. physiol. Chem.*, **5**, 1881.
[8] Miquel: *Ann. de Micrographie*, **1**, 414, 417, 506, 522; **2**, 13, 53, 122, 145, 367, 488; **3**, 275, 305.
[9] Leube: Virchow's *Archiv.*, **100**, 540.

Laureau,[1] Warrington,[2] and a number of others. These investigators find that urea and uric acid are readily and completely fermented by a number of common bacteria, forming ammonia and carbonic acid, which combine and remain in solution unless further acted upon by other bacteria.

Nitrification.—The oxidation of ammonia to nitrites and nitrates, has usually been considered to be the function of a specific class of organisms which will not grow on ordinary culture media, and hence cannot be included in the scope of the present study. The classical work of Winogradsky[3] and Warrington[4] with this class of organisms is too well known to require review here. At the same time there is some experimental evidence, more or less authentic, which would point to the fact that certain common species, not belonging to Winogradsky's group of nitrifying bacteria, are, under certain conditions, able to accomplish the oxidation of ammonia to nitrites and nitrates.

In 1886, Celli and Zucco[5] and Heraeus[6] succeeded in isolating from water by the usual methods a number of species of bacteria which appeared to have feeble nitrifying powers. In 1895, Burri and Stutzer[7] isolated from soil an organism with nitrifying properties, and two years later Stutzer and Hertleb[8] offered a further confirmation of the earlier work of Burri and Stutzer in which they claimed not only to have made the nitrifying organism grow on all ordinary culture media, but also stated their belief that this organism had a pleo-morphic habit, changing its form and character under different conditions. Much doubt has been cast on the purity of the cultures with which these investigators worked, and Fraenkel[9] claims to have isolated from Burri and Stutzer's cultures eleven different species.

In 1896 Woodhead[10] isolated from sewage a number of different

[1] Ladereau: *Compt. Rend.*, **100**, 1252 (1885).
[2] Warrington: *Cent. f. Bakt.*, **6**, 498 (1888).
[3] Winogradski: *Ann. de l'Inst. Pasteur*, **4**, 213, 357 (1890); **5**, 577, 921 (1891).
[4] Warrington: *J. Chem. Soc.* (London), 1891, p. 484.
[5] Celli and Zucco: *Rendiconta della R. Acc. dei. Lincei*, 1886.
[6] Heraeus: *Landw. Jahrb.*, 1887; *Landw. Versuchsst.*, **38** (1888).
[7] Burri and Stutzer: *Cent. f. Bakt.*, **1** (2), 721, 749 (1895).
[8] Stutzer and Hertleb: *Ibid.*, **3** (2), 6, 54, 161 235, 311, 351 (1897).
[9] Fraenkel: *Cent. f. Bakt.*, **4** (2) Nos. 1 and 2 (1898).
[10] Woodhead: Quoted by Rideal, "Bacterial Purification of Sewage," p. 54 (1900).

species which grew well on ordinary culture media, some of them being denitrifying forms and others being able to oxidize nitrites to nitrates.

Richter[1] isolated a micrococcus which reduced nitrates to nitrites and was also able to oxidize urea to nitrites. Furthermore, we must consider that the symbiosis of bacteria, as regards action on nitrogenous bodies, has been little studied. Indeed, it is an open question in the minds of many sewage and soil bacteriologists as to whether the so-called nitrifying group of bacteria are the sole cause of nitrification. That there is some ground for this doubt is instanced by many experiments in sewage treatment in which sterile materials inoculated with pure cultures of these types have failed to nitrify, or at best, have nitrified only very slowly when dosed with ammonia solutions or with sterile sewage, while control filters of the same material have nitrified unsterilized sewage rapidly and completely.

As to the conditions governing nitrification there is some diversity of opinion. The earlier observers uniformly considered that nitrification was essentially an aerobic or oxidizing process. Holdefleiss[2] on the other hand obtained results in his experiments which would warrant the belief that nitrification may often take place under strictly anaerobic conditions. Further evidence of this has not been forthcoming, however, and the results obtained from the operation of sewage filters would indicate that efficient aeration is necessary, if nitrification is to continue.

Leme,[3] Pickard,[4] and others have shown that an excess of organic matter tends to check or prevent nitrification. Davy[5] observes that the reduction in nitrification is especially marked when the excess of organic nitrogen is of animal origin. The sudden stoppage of nitrification in sewage filters when continually overdosed, and the return of this action when the quantity of organic matter applied has been reduced within the proper limits, are common knowledge to all who have had experience in the operation of sewage disposal works. The conditions affecting nitrification by sewage filters and the amount of nitrogen which these filters will nitrify regularly have been exhaustively studied

[1] Richter: Quoted by Rideal, *Loc. cit.*, p. 91.
[2] Holdefleiss: "Der Stallmist," Breslau, 1889.
[3] Leme: *Naturwis. Rund.*, **5**, 291 (1890).
[4] Pickard: *Compt. Rend.*, **114**, 490 (1892).
[5] Davy: *J. Chem. Soc.* (London), 1879, p. 429.

at the Experiment Station and will be found discussed in the annual reports of the Massachusetts State Board of Health since 1890, under the chapters on filtration of sewage.

Nitrogen Liberation.—There is considerable difference of opinion as to whether or not free nitrogen is formed in the breaking-down of peptones and amino acids. The results of Immendorff,[1] Kellner,[2] Tacke,[3] Ehrenberg,[4] Schlösing,[5] Muntze Girard and Schneidewind,[6] Dietzell,[7] and Pfeiffer,[8] would appear to support the view that no free nitrogen is evolved when the reactions take place under strictly anaerobic conditions. On the other hand, Wollney[9] takes the stand that nitrogen may be given off in putrefaction, and quotes the results of König and Kiesow,[10] Dietzell,[11] Morgan and König[12] to support his arguments. Zoja[13] found that elastin, when fermented under anaerobic conditions, gave off free nitrogen. Wood and Wilcox[14] found that *B. furfuris*, which they believed to be the cause of putrefaction in the tanning industry, liberated nitrogen gas from nitrogenous matter in the presence of starch under anaerobic conditions. Hugonenq and Doyon[15] found that under anaerobic conditions *B. typhosus* and *B. tetanus* evolved considerable amounts of free nitrogen from nitrogenous solutions. The composition of gases given off from putrefying sewage in septic tanks has been carefully studied during the past few years by a number of observers. Although the percentage composition of the gases given off by septic tanks in different places has varied widely, in every case a considerable percentage of nitrogen has been reported, some of the results being as follows: At Lawrence, Mass.,[16] the gases from two different tanks contained 16 per cent.

[1] Immendorff: *Landw. Jahrb.*, **21**, 281 (1892).
[2] Kellner: *Ztschr. physiol. Chem.*, **12**, 95 (1887).
[3] Tacke: *Landw. Jahrb.*, **16**, 917 (1887).
[4] Ehrenberg: *Ztschr. physiol. Chem.*, **12**, 145, 438 (1887).
[5] Schlösing: *Compt. Rend.*, **109**, 835 (1889).
[6] Muntze Girard and Schneidewind: *Journal f. Landw.*, **45**, 173.
[7] Dietzell: *Landw. Versuchsst.*, **48**, 177 (1896).
[8] Pfeiffer: *Ibid.*, p. 243.
[9] Wollney: "Die Zersetzung der Organischen Stoffe," pp. 12, 13.
[10] König and Kiesow: *Landw. Jahrb.*, **2**, 107 (1873).
[11] Dietzell: *Ztschr. des Landw. Vereins* in Bayern, March, 1882.
[12] Morgan and König: *Landw. Versuchsst.*, **30**, 199, 216 (1884).
[13] Zoja: *Ztschr. physiol. Chem.*, **23**, 236 (1897).
[14] Wood and Wilcox: quoted by Rideal, *Loc. cit.*, p. 72.
[15] Hugonenq and Doyon: *Ann. Chem. Phys.*, **7**, 45 (1898).
[16] Thirty-second Annual Report, Mass. Board of Health, 1900, p. 392.

and 19 per cent. of free nitrogen, respectively. At Andover, Mass.,[1] the gas contained 61 per cent. nitrogen. At Worcester, Mass., Kinnicutt[2] found the gas to contain about 17 per cent. of nitrogen. Rideal[3] found that two samples of gases given off from the tank at Exeter, England, contained 39 and 61 per cent. of free nitrogen respectively. Fowler[4] reports the gas from the tank at Manchester, England, to contain 16 per cent. of free nitrogen.

There is also a difference of opinion as to whether nitrogen is liberated in decay, that is, when the decomposition takes place in the presence of air. Ehrenberg,[5] by a long series of experiments in which he made careful measurements of the gases evolved, decided that no gaseous nitrogen was evolved. Hufner[6] also coincides in the opinion that no nitrogen is liberated in decay proper. Kellner and Yoskii[7] found that the loss of nitrogen during decay was very small, even when the experiment was carried over a long period. On the other hand, the results obtained by Tacke[8] led him to believe "that in the oxidation of ammonia, as well as in the reduction of nitric acid to ammonia, conditions may arise by which two nascent nitrogen atoms can combine into molecular nitrogen and escape from the decaying mass." Chabrier[9] found that small amounts of nitrogen are always liberated during nitrification, and his observations have been confirmed by Boussingault,[10] by Pickard,[11] and more recently by Godlewski.[12] Schneidewind,[13] Pfeiffer,[14] and Stutzer and Hertleb[15] all furnish evidence that losses of free nitrogen are likely to occur.

Gerlach and Vogel[16] isolated from soil a number of bacteria

[1] Thirty-second Annual Report, Mass. Board of Health, 1900, p. 392.
[2] Kinnicutt: Quoted by Rafter, "Treatment of Septic Sewage," 1904, p. 80.
[3] Rideal: Interim Rep. Royal Sew. Comm., **2**, 247, Q. 4135 (1902).
[4] Fowler: *Ibid.*, p. 453, Q. 8401.
[5] Ehrenberg: *Ztschr. physiol. Chem.*, **11**, 439 (1887).
[6] Hufner: *J. prakt. Chem.*, 1876, p. 292.
[7] Kellner and Yoskii: *Ztschr. physiol. Chem.*, **11**, 95 (1887).
[8] Tacke: *Landw. Jahrb.*, **16**, 917 (1887).
[9] Chabrier: *Compt. Rend.*, **67**, 1031.
[10] Boussingault: *Ibid.*, **77**, 1480.
[11] Pickard: *Jour. de Agr. Pract.*, **2**, 273 (1884).
[12] Godlewski: *Cent. f. Bakt.*, **2**, 458 (1896).
[13] Schneidewind: *Jour. f. Landw.*, **45**, 176 (1887).
[14] Pfeiffer: *Landw. Versuchsst.*, **48**, 202 (1896).
[15] Stutzer and Hertleb: *Cent. f. Bakt.*, **44** (2), 31 (1898).
[16] Gerlach and Vogel: *Ibid.*, **7** (2), 609 (1901).

which were able to transform soluble inorganic salts into insoluble organic nitrogen, but when organic nitrogen was present this transformation into proteids was always accompanied by a loss of free nitrogen.

Rogoyski[1] arrived at similar conclusions concerning the simultaneous liberation of nitrogen and the fixation of soluble nitrogen as proteids, and also determined that the proteid nitrogen so formed appeared to be non-putrescible and readily nitrifiable without intermediate conversion into ammonia. This latter point is worthy of further study, bearing, as it does, on the storage of nitrogen in sewage filters at times and the ultimate disappearance of this stored nitrogen with the appearance of large amounts of nitrates and nitrites in the filter effluents.[2] Proteids of this class may also form a large percentage of the organic matter in the sediment in the effluents from filters of coarse materials operating at high rates, which, although usually very turbid and containing considerable suspended organic matter, have been repeatedly proved to be non-putrescible.[3] Berthelot,[4] studying the volatility of the ammonia from soil, found that when there was a loss of ammonia extensive loss of free nitrogen occurred at the same time. The same author observes that the activity of bacteria in soils may lead to a very considerable loss of nitrogen either as ammonia or as elementary nitrogen, and the evolution of free nitrogen is independent of the presence or absence of nitrates. Lipman[5] describes an interesting experiment in which he proved that *B. pyocyaneus* caused a greater loss of nitrogen in solution as the surface of the solution exposed to the air was increased. The better aeration thus produced was evidently the cause of the greater loss, although he did not determine definitely whether the loss was due to increased volatilization of the ammonia, or, as was more likely, to the increased oxidation and setting-free of elementary nitrogen. Rideal[6] has calculated the amount of oxygen necessary to completely oxidize certain typical organic compounds either to ammonia or to elementary nitrogen, and it is significant that more oxygen is re-

[1] Rogoyski: *Ann. Agr.*, **26**, 121, 140 (1900).
[2] 26th Annual Report Mass. Board of Health, 1894, p. 486.
[3] 33rd Annual Report Mass. Board of Health, 1901, p. 372.
[4] Berthelot: *Chemie Vegitale et Agricole*, p. 160.
[5] Lipman: Annual Report N. J. Agr. Expt. Sta., 1903, p. 226.
[6] Rideal: "Bacterial Purification of Sewage," 1900, p. 73.

quired for the second reaction than for the first. This would go to prove that nitrogen is more likely to be set free under aerobic than under anaerobic conditions.

Fixation of Atmospheric Nitrogen.—As to the fixation of atmospheric nitrogen in organic solutions there is also considerable controversy and the available data is very meagre. Laurent[1] found that certain algae in symbiosis with bacteria were able to fix nitrogen in sand which was exposed to the air and sunlight. This observation was confirmed by Bouilhac,[2] who decided that the bacteria were the cause of the fixation of the nitrogen, the algae merely furnishing the food supply for the bacteria, and this view has more recently been substantiated by the experiments of Kruger and Schneidewind.[3] Nobbe and Hitner[4] observed that there was a fixation of nitrogen in soils and attributed this action to the agency of micro-organisms. Stoklasa and Vitek[5] believed that many of the denitrifying bacteria under certain conditions have the power to fix atmospheric nitrogen, basing their belief on the fact that in their experiments *B. ellenbachiensis* fixed atmospheric nitrogen in solutions which contained no nitrates. Hiltner[6] found in soil, inoculated with denitrifying bacteria, that the yield was greater than where the soils were sterile. Lipman[7] found in soils containing small amounts of nitrogenous matter, that *B. pyocyaneus*, and a number of other denitrifying bacteria were able to fix atmospheric nitrogen.

Beijerinck[8] found that a greater fixation of atmospheric nitrogen occurred in solutions which contained small amounts of organic nitrogen, and this finding was later confirmed by Lipman's[9] experiments. Chester[10] has recently proved without a shadow of doubt that a number of species of bacteria common in sewage are, under certain conditions, able to fix large amounts of atmos-

[1] Laurent: *Ann. de l'Inst. Pasteur*, **6**, 832 (1892).
[2] Bouilhac: *Compt. Rend.*, **123**, 828 (1896).
[3] Kruger and Schneidewind: *Landw. Jahrb.*, **29**, 711, 784 (1901).
[4] Nobbe and Hitner: *Landw. Versuchsst.*, **45**, (1894).
[5] Stoklasa and Vitek: *Cent. f. Bakt.*, **7** (2), 257 (1901).
[6] Hiltner: *Ibid.*, **9** (2), 73 (1902).
[7] Lipman: Annual Report N. J. Agr. Expt. Sta., 1903, p. 230.
[8] Beijerinck: *Cent. f. Bakt.*, **9** (2), 3 (1902).
[9] Lipman: *Loc. cit.*, 1902, p. 231.
[10] Chester: Bull. 66, Del. Agr. Expt. Sta., 1904, pp. 8 to 13.

pheric nitrogen. In addition, there is much recent literature concerning the fixation of nitrogen by bacteria in root tubercles, but the indications at present are that these bacteria are all of one species, and that they do not come within the scope of the sewage analyst.

Denitrification.—In the nitrate solution, besides the peptone and the atmospheric nitrogen as sources of nitrogen, we have present the nitrates, and the changes which may take place are more complex and subject to variation. Here we may have, as in the peptone solution, the fixation of atmospheric nitrogen and the conversion of the peptone into ammonia or free nitrogen or both, and we may also have the reduction of the nitrates to nitrites, to ammonia, to free nitrogen, and we may have the formation of nitrous and nitric oxides. Furthermore, we may have secondary reactions between the nitrites or the lower oxides of nitrogen and the amino acids and amines. The literature on denitrification is particularly rich, owing to its great significance in agriculture.

As early as 1862 Gopplesröder[1] observed that in rich soils denitrification usually took place. In 1867 Froehde[2] observed that a reduction of nitrates frequently occurred when putrefying organic matter was present. In 1868 Schoenbein[3] noticed that many fungi (bacteria?) were able to reduce nitrates to nitrites, and offered the presence of nitrites in drinking water as direct evidence of the presence of micro-organisms. In 1871 Meusel[4] attributed the reduction of nitrates in water to the action of bacteria. Pesci[5] observed that the reduction of nitrates was much more rapid in liquids than in dry or slightly moist material. Gayon and Dupetit,[6] in 1882, observed that in river water containing small amounts of nitrates the nitrates were quickly reduced to ammonia. Deherain and Maquenne[7] and Springer[8] attributed the reduction of nitrates to the agency of anaerobic bacteria which either reduced the nitrates to lower oxides of nitrogen or to free nitrogen. Heraeus,[9] in 1886, isolated from water two species which reduced

[1] Gopplestroder: *Pogg. Ann.*, **115**, 125 (1862).
[2] Froehde: *J. prakt. Chem.*, **102**, 46 (1867).
[3] Schoenbein: *Ibid.*, **105**, 211 (1868).
[4] Meusel: *Ann. Chem. Phys.*, **23**, 161 (1871).
[5] Pesci: *Ber. d. chem. Ges.*, **8**, 259.
[6] Gayon and Dupetit: *Compt. Rend.*, **95**, 544, 365 (1882).
[7] Deherain and Maquenne: *Ibid.*, p. 1365.
[8] Springer: *Ber. d. chem. Ges.*, **16** (1883).
[9] Heraeus: *Ztschr. f. Hyg.*, **1**, 193 (1886).

nitrates to nitrites quickly. Blasi and Fravoli,[1] in 1888, studied twenty-seven species which they had isolated from soil and found that in the majority of instances these species rapidly reduced nitrates to nitrites, and then slowly destroyed the nitrites, although they fail to state what the end-product was. Giltay and Aberson,[2] in 1892, found common in both soil and the atmosphere two organisms, both of which were able to reduce nitrates completely with a liberation of free nitrogen. Eugnow,[3] Burri,[4] Herfeldt and Stutzer, and Schirokokh[5] all isolated and studied species which reduced nitrates. Sewerin[6] studied twenty-nine species, twenty of which were able to reduce nitrates more or less completely. Maasen,[7] in 1902, found that of 109 species of bacteria he examined, eighty-five were able to produce nitrites in solutions containing nitrates. The writer,[8] in a previous paper, reported that of 5,300 cultures of bacteria isolated at the Experiment Station, 85 per cent. were able to reduce nitrates more or less completely, and of 46 different species described at that time thirty-five reduced nitrates to nitrites.

Jensen[9] states that denitrifying bacteria are usually present in the excreta from herbivorous animals, but that they are rare in the effluvia of carnivorous animals. Chester[10] shows that denitrification may take place either under aerobic or anaerobic conditions, confirming the results of Stutzer and Maul,[11] and Boname,[12] who found that denitrification was less rapid under aerobic than under anaerobic conditions. On the other hand, Pfeiffer, Franke, Gotze and Thumann[13] obtained results which led them to believe that denitrification was more rapid when there was free access of air. Frankland[14] concluded from a study of thirty-two well-

[1] Blasi and Fravoli: *Gaz. chim. Ital.*, Palermo, **19** (1888).
[2] Giltay and Aberson: *Abs. in Cent. f. Bakt.*, **12**, 864 (1893).
[3] Eugnow: *Cent. f. Bakt.*, **3**, (2) 504 (1896).
[4] Burri, Herfeldt and Stutzer: *Ibid.*, **1**, 284 (1895).
[5] Schirokokh: *Ibid.*, **2** (2), 204 (1895).
[6] Sewerin: *Ibid.*, **3** (2), 504 (1896).
[7] Maasen: *Ibid.*, **8** (2), 152 (1902).
[8] Gage: 33rd Annual Report Mass. Board of Health, 1901, pp. 401, 419.
[9] Jensen: *Cent. f. Bakt.*, **4** (2), 448 (1898).
[10] Chester: Bull. 98, Penn. Dept. Agr., 1902, p. 64.
[11] Stutzer and Maul: *Cent. f. Bakt.*, **2** (2), 473 (1896).
[12] Boname: Ann. Sta. Agronomic, Mauritius, 1896, p. 74.
[13] Pfeiffer, Franke, Gotze and Thurmann: *Landw. Versuchsst.*, **98**, 189, 245.
[14] Frankland: *J. Chem. Soc.* (London), 1888, p. 372.

known species of water bacteria, more than half of which were able to reduce nitrates to nitrites more or less completely, that the action of these organisms was the same whether they were grown under aerobic or anaerobic conditions.

Stutzer and Jensen[1] showed that a certain amount of organic matter was necessary in solutions for cultures of bacteria to actively reduce nitrates, and the conclusions of these writers have been confirmed by experiments of Kruger,[2] and Wood,[3] Jeannel[4] found that the reduction of nitrates was more rapid when carbohydrates were present.

Liberation of Nitrogen from Nitrated Solutions.—There is some experimental evidence to show that nitrogen is liberated from nitrated solutions, and that in some instances this liberation is due to secondary reaction between the amides and amino acids, and some of the oxides of nitrogen.

As early as 1867 Dr. Angus Smith[5] observed that a reduction of nitrates accompanied by a loss of nitrogen occurred in decomposing sewage. Lipman[6] found that all of the five cultures which he studied, *B. subtilis*, *B. fluorescens*, *B. megatherium*, *B. pyocyaneus* and *B. New Jersey*, liberated nitrogen from organic solutions containing nitrates, although one of the cultures failed to reduce nitrates.

Gerlach and Vogel[7] isolated from soil and manure a number of species of bacteria which, in solutions in which potassium nitrate was the only source of nitrogen, were able to reduce nitrates to nitrites. Later the nitrites disappeared and determinations of total nitrogen showed that there was a loss of nitrogen, although no ammonia had been formed during any portion of the experiment.

Grimbert[8] found that while both *B. coli* and *B. typhosus* are able to liberate nitrogen from nitrated solutions, these species do not liberate free nitrogen unless amido compounds are present, and when nitrogen is liberated by these organisms from

[1] Stutzer and Jensen: *Cent. f. Bakt.*, **2** (2), 2, 7 (1895).
[2] Kruger: *Landw. Jahrb.*, **29**, Nos. 4 and 5 (1900).
[3] Wood: London Rep. Agr. Ed. and Res., 1899, p. 124.
[4] Jeannel: *Compt. Rend.*, **75**, 1244 (1872).
[5] Smith: Quoted by Aikman, "Manures and Manuring," 1867, p. 177.
[6] Lipman: *Loc. cit.*, 1902, p. 222.
[7] Gerlach and Vogel: *Cent. f. Bakt.*, **7** (2), 609 (1901).
[8] Grimbert: *Ann. de l'Inst. Pasteur*, **13**, 67 (1898).

a nitrated medium the volume of nitrogen is always about double the amount of nitrogen lost from the nitrates, thus confirming a previous observation of Hugonenq and Doyon,[1] that *B. coli* reduces nitrates, setting free nitrogen and utilizing the oxygen to oxidize carbonaceous matter.

Ampolla and Gatino[2] studied an organism which reduced nitrates completely, forming a gas which consisted of 85 per cent. of nitrogen and 15 per cent. of carbon dioxide. These authors also found that denitrification is more rapid in alkaline than in acid solutions, and that relatively small amounts of acid were able to prevent losses of nitrogen. That this does not hold true with the organic acids is shown by the experiments of Schlösing,[3] who established the fact that nitrogen is always liberated when the lactic fermentation of sugars occurs in the presence of nitrates.

Deherain and Maquenne[4] studied the gases evolved during denitrification and found that they contained free nitrogen, carbon dioxide and nitrous oxide.

Gayon and Dupetit[5] observed that nitrogen was evolved during denitrification and that the presence of organic nitrogen was necessary for this evolution. They were led to believe that the organic nitrogen is decomposed into ammonia and amines, and that the liberation of free nitrogen is the result of secondary reaction between the amido derivatives of the organic matter and the reduction products of the nitrates. By properly controlling the composition of the fermenting solutions they were able to produce a liberation of nitrogen with or without the admixture of nitrous oxide.

Ampolla and Ulpianni[6] describe two species which changed nitrates in the presence of organic matter into free nitrogen without the intermediate production of nitrites. Frankland[7] found that although *B. aquatilis* was unable to cause a reduction of nitrates to nitrites, yet there was a considerable loss of nitrates from solutions in which it was cultivated.

[1] Hugonenq and Doyon: *Ann. Chem. Phys.*, **7**, 45 (1898).
[2] Ampolla and Gatino: *Cent. f. Bakt.*, **2**, 670 (1896).
[3] Schlösing: *J. Pharm. Chem.*, **8** (4), 213 (1868).
[4] Deherain and Maquenne: *Ann. Agron.*, **9**, 5 (1882).
[5] Gayon and Dupetit: Sta. Agr. de Bordeaux, 1886.
[6] Ampolla and Ulpianni: *Gaz. chim. Ital.*, **28** (1), 410 (1898).
[7] Frankland: *J. Chem. Soc.* (London), 1888, p. 391.

Burri and Stutzer[1] observed that *B. denitrificans II* was able to liberate about 90 per cent. of the nitric nitrogen from certain nitrated solutions, the remaining nitrogen being rendered insoluble. At the start they found that this organism was aerobic, but after denitrification was once started it was able to develop under anaerobic conditions, indicating that the organism was able to use the oxygen set free from the nitrates in its own life cycle.

The foregoing presents a brief and at the same time comprehensive review of the more important literature on bacteriolysis so far as it appears to be directly applicable to the problems confronting the sewage disposal expert, and to the subject-matter of the present paper.

While a number of excellent reviews of different portions of the literature have appeared in the past, nearly all of these, compiled by agricultural bacteriologists, have contained much matter which at present seems to be of no moment in sewage treatment, and none of them have emphasized the points which are of paramount importance to the practical sanitary expert. The viewpoints of the soil bacteriologist and of the man dealing with the disposal of the sewage of large cities are diametrically opposite, the problem of the former being the conservation of nitrogen and the bringing of that nitrogen to the cultivated field in such a form that it shall be stable and readily assimilated by growing plants, while the latter desires to get rid of the nitrogenous matters as quickly and as cheaply as possible. However deplorable the liberation of nitrogen may be in agriculture, and however desirable the assimilation of atmospheric nitrogen, in sewage treatment this same fixation of nitrogen is to be prevented whenever possible, while the liberation of large quantities of organic nitrogen as an inoffensive gas would be of immense advantage.

DISCUSSION OF THE EXPERIMENTAL DATA.

In discussing the results obtained from the study of the change in the nitrogen content of the experimental solutions by the selected cultures, the data have been collected in two tables, Table II showing the progressive change induced by each culture as determined by analyses on successive days, and Table III showing the reduction in the amount of the various nitrogenous constituents

[1] Burri and Stutzer: *Cent. f. Bakt.*, **1**, (2) 721, 749 (1895).

and the gain or loss of nitrogen during the entire period of the experiment. In considering the progressive change in the nitrogen content of the solutions, as shown by the results in Table II, it will simplify matters somewhat to take up the various reactions by types rather than to discuss the phenomena of each culture separately.

Ammonification.—The amount of ammonia produced in the peptone solution has varied widely with the individual cultures. Of the twenty cultures included in the table, No. 33 showed no ammonification whatever. Five cultures, Nos. 11, 17, 23, 26, and 38, showed only traces of ammonia, *i. e.*, less than 0.5 part per 100,000, and No. 4 showed only 0.7 part. The maximum amount of ammonia produced by any one culture was 18 parts, this being recorded for culture No. 10 on the twentieth day. Four cultures, Nos. 10, 13, 16 and 24, produced over 4 parts of ammonia. As to the rate of ammonification, after two days' growth none of the cultures showed any traces of ammonia. After four days four cultures had begun to ammonify, these being Nos. 10, 24, 31 and 40. On the sixth day three more cultures, Nos. 18, 22 and 41, had begun to produce ammonia. On the tenth day eleven of the twenty cultures showed ammonia production, cultures Nos. 9, 13, 16 and 29 having come into the fold, and on the thirteenth day two more cultures, Nos. 1 and 7, were added to the list.

Denitrification.—In the reduction of nitrates the various cultures have shown many peculiarities, in some cases a steady decrease in the amount of nitrates being noticed, while with other cultures the reduction was spasmodic and erratic. Six of the cultures, Nos. 1, 13, 16, 23, 26 and 38, failed to reduce nitrates at any time in the period during which they were under examination, although culture No. 38 produced small amounts of both nitrites and ammonia in the nitrate solution. Four of the cultures, Nos. 4, 10, 11 and 18, reduced all of the nitrates within the period of incubation, while four more, Nos. 7, 9, 17 and 22, reduced over 50 per cent. of the nitrates. As to the rate of denitrification, two of the cultures, Nos. 10 and 31, show loss of nitrates on the second day. On the fourth day five more cultures showed nitrate reduction, these being Nos. 7, 18, 22, 40 and 41. On the sixth day culture No. 11 showed denitrification, and on the tenth day culture No. 33 began to be

active. Four more cultures, Nos. 4, 9, 24 and 29, showed up on the thirteenth day, and by the seventeenth day culture No. 17 had begun to reduce.

Nitrite Production.—As with the reduction of nitrates, the production of nitrites by the various cultures has been subject to considerable variation. Four of the cultures, Nos. 10, 13, 16, and 23, failed to produce nitrites. Of these, culture No. 10 is of special interest, because, although this culture reduced the nitrates completely, the reduction did not go through the nitrite stage. Three of the cultures, Nos. 1, 26 and 33, produced only traces of nitrites, that is, less than 0.5 part, and culture No. 38 produced less than 1 part. Culture No. 38 is especially interesting, because, although the nitrates were not reduced by the culture, nitrites and ammonia were formed in the nitrate solution in small amounts. The results from cultures Nos. 29, 31 and 41 are interesting, as more nitrites were produced than there was loss of nitrate, and cultures Nos. 29 and 40 showed nitrite production before any reduction of nitrates was noted. These results may be taken as evidence that in the nitrate solution some oxidation or nitrification may have taken place, although in no case were nitrites found in the peptone solution. One of the cultures, No. 11, produced nitrites equivalent to 100 per cent. of the total amount of nitrates reduced, and seven more of the cultures, Nos. 4, 7, 9, 17, 18, 22 and 40, produced nitrites equivalent to 50 per cent. or more of the total amount of nitrates reduced. Of the cultures producing more than 1 part of nitrites, Nos. 31 and 41 gave reactions on the second day, and No. 40 on the fourth day. On the sixth day, cultures Nos. 7, 18 and 22 had begun to produce nitrites actively, and on the tenth day cultures Nos. 9, 11 and 29 were added to the list. Culture No. 4 did not show any great amount of nitrites until the thirteenth day, and cultures Nos. 17 and 24 did not show active nitrite production until the seventeenth day.

Reduction of Nitrates to Ammonia.—The previously discussed functions, the ammonification of peptone, the reduction of nitrates, and the production of nitrites are functions which can be accurately determined and of which we can speak positively in quoting results. As to the production of ammonia from the nitrates, however, we cannot speak so conclusively owing to the indirect method of determination, *i. e.*, by the subtraction of

the ammonia formed in the peptone solution from the total amount of ammonia formed in the nitrated peptone solution, and to the fact that the same culture may not ammonify the peptone in the same ratio in the two solutions, and while we may draw inferences, our results must always be open to criticism and doubt. Nevertheless, some of the results obtained have apparently been of considerable significance. The estimated amounts of ammonia formed from the nitrates, as shown in Table II, are much more erratic and subject to variation than are the figures of the directly determined functions. Eight of the cultures, Nos. 1, 7, 13, 16, 18, 22, 23 and 29, did not show any apparent production of ammonia from the nitrates. Five of the cultures, Nos. 4, 9, 10, 11 and 24, produced ammonia equivalent to more than 50 per cent. of the total amount of nitrates reduced. Cultures Nos. 4, 17 and 24 produced more ammonia during certain periods of the time that they were under examination than was the total amount of nitrates reduced, and one culture, No. 38, produced ammonia, although no reduction of the nitrates occurred. The cause of this overproduction of ammonia is difficult to explain. It may have been due to secondary reactions between the nitrites or other oxides of nitrogen, and the amides or amino acids; it may have been due to the direct fixation of atmospheric nitrogen in the form of ammonia, and it may have been due to an invigorating action of the nitrates on the bacteria themselves, causing them to break down the peptone more completely in the solution containing nitrates than they did in the plain peptone solution. Five of the cultures, Nos. 26, 33, 38, 40 and 41, produced less than 1 part of ammonia; four of the cultures, Nos. 9, 10, 17 and 31, produced between 1 and 3 parts of ammonia, and three of the cultures, Nos. 4, 11 and 24, produced more than 3 parts of ammonia.

Undetermined Nitrogen from Nitrates.—The figures given in this column, as previously explained, are of very doubtful significance, including, as they do, the sum of all the errors in the other determinations. Nevertheless, the results are more or less significant as indicating whether other oxides of nitrogen than nitrites had been formed, which oxides would not be determined by the analytical methods employed, and also as furnishing additional evidence as to the liberation of nitrogen from solutions containing nitrates. Eleven of the cultures did not show losses

of nitrates which could not be accounted for either as nitrites or ammonia, while six of the cultures, Nos. 7, 10, 11, 18, 22 and 23, showed losses, or undetermined nitrogen, amounting to over 50 per cent. of the total amount of nitrates reduced. With cultures Nos. 11, 18, 22, 23 and 40 the largest amounts of undetermined nitrogen occurred during the earlier or intermediate portions of the period of incubation, these amounts decreasing or entirely disappearing towards the end of the incubation period. This would indicate oxides of nitrogen or at least that the nitrogen was in some form which was not determinable, but which was afterwards changed to a form which we were able to determine. With cultures Nos. 11, 33 and 40 the indications are that those losses occurred between the nitrites and ammonia. With cultures Nos. 18 and 22, however, judging from the fact that a very rapid reduction of nitrates occurred, a large percentage of which could not be accounted for either as nitrites or ammonia, but which percentage was later reduced as the nitrites increased, would appear to indicate that some intermediate product between the nitrates and nitrites has been formed. Such a product, as far as we have been able to discover, has never been noted by previous observers, and if the results are not in error, is of much interest. In addition to these cultures three others, Nos. 7, 9 and 31, showed losses or undetermined nitrogen which it would appear was liberated as elementary nitrogen. This is especially marked with culture No. 7, in which the loss of nitrogen increased in direct ratio with the time of incubation.

TABLE II.—SHOWING THE PROGRESSIVE CHANGE IN THE NITROGEN CONTENT OF PEPTONE SOLUTION AND NITRATED PEPTONE SOLUTION DUE TO THE GROWTH OF PURE CULTURES OF BACTERIA.

		Nitrogen—parts per 100,000.				
				Ammonia from		
Culture number.	Days.	Nitrates, total reduction.	Nitrites from nitrates.	nitrates.	peptone.	Undetermined nitrogen from nitrates.
1.	2.	3.	4.	5.	6.	7.
N–1	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.2	0.0
	6	0.0	0.0	0.0	0.2	0.0
	8	0.0	0.0	0.1	0.2	0.0
	10	0.0	0.0	0.2	0.3	0.0
	13	0.0	0.0	0.0	1.0	0.0
	17	0.0	0.1	0.0	2.0	0.0
	20	0.0	0.1	1.7	2.1	0.0

Culture number.	Days.	Nitrogen—parts per 100,000				
		Nitrates, total reduction.	Nitrites from nitrates.	Ammonia from nitrates.	Ammonia from peptone.	Undetermined nitrogen from nitrates.
1.	2.	3.	4.	5.	6.	7.
N-4	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.1	0.0
	6	0.0	0.0	0.0	0.1	0.0
	8	0.0	0.0	0.0	0.2	0.0
	10	0.0	0.1	0.2	0.3	0.0
	13	3.0	2.3	0.8	0.6	0.0
	17	6.0	5.5	5.5	0.5	0.0
	20	6.0	5.0	6.9	0.6	0.0
N-7	2	0.8	0.8	0.0	0.1	0.0
	4	1.2	0.9	0.0	0.2	0.3
	6	1.7	1.3	0.0	0.3	0.4
	8	2.2	1.6	0.0	0.5	0.6
	10	2.5	1.8	0.0	0.7	0.7
	13	2.5	1.7	0.0	1.1	0.8
	17	3.0	1.6	0.0	2.0	1.4
	20	3.5	1.6	0.0	2.2	1.9
N-9	2	0.3	0.3	0.0	0.1	0.0
	4	0.4	0.4	0.0	0.2	0.0
	6	0.4	0.4	0.0	0.4	0.0
	8	0.4	0.6	0.0	0.7	0.0
	10	0.5	1.2	0.0	1.0	0.0
	13	1.2	0.6	0.6	0.1	0.0
	17	2.5	1.5	0.0	3.2	1.0
	20	5.3	3.0	1.5	2.3	0.8
N-10	2	1.0	0.0	0.6	0.5	0.4
	4	2.7	0.0	1.0	1.5	1.7
	6	2.7	0.0	1.1	2.4	1.6
	8	2.7	0.0	0.0	2.5	2.7
	10	2.7	0.0	2.6	4.0	0.1
	13	2.7	0.0	1.0	10.0	1.7
	17	2.7	0.0	2.4	7.4	0.3
	20	2.7	0.0	0.0	18.0	2.7
N-11	2	0.2	0.2	0.0	0.0	0.0
	4	0.2	0.2	0.0	0.0	0.0
	6	1.5	0.2	0.0	0.0	1.3
	8	1.7	0.7	0.3	0.0	0.7
	10	1.8	1.5	1.1	0.1	0.0
	13	5.0	3.4	1.2	0.2	0.4
	17	6.0	6.0	3.3	0.2	0.0
	20	6.0	2.8	4.5	0.5	0.0

Culture number. 1.	Days. 2.	Nitrogen—parts per 100,000. Nitrates, total reduction. 3.	Nitrites from nitrates. 4.	Ammonia from nitrates. 5.	Ammonia from peptone. 6.	Undetermined nitrogen from nitrates. 7.
N–13	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.2	0.0
	6	0.0	0.0	0.0	0.2	0.0
	8	0.0	0.0	0.0	0.3	0.0
	10	0.0	0.0	0.0	1.1	0.0
	13	0.0	0.0	0.0	2.9	0.0
	17	0.0	0.0	0.0	4.5	0.0
	20	0.0	0.0	0.0	4.2	0.0
N–16	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.0	0.0
	6	0.0	0.0	0.0	0.5	0.0
	8	0.0	0.0	0.0	1.2	0.0
	10	0.0	0.0	0.0	3.0	0.0
	13	0.0	0.0	0.0	5.5	0.0
	17	0.0	0.0	0.0	4.9	0.0
	20	0.0	0.0	0.0	7.5	0.0
N–17	2	0.1	0.1	0.0	0.0	0.0
	4	0.4	0.4	0.0	0.2	0.0
	6	0.5	0.5	0.1	0.2	0.0
	8	0.6	0.7	0.2	0.2	0.0
	10	0.5	0.7	0.2	0.2	0.0
	13	0.7	0.9	0.7	0.3	0.0
	17	1.6	1.4	2.0	0.2	0.0
	20	2.3	2.2	2.8	0.2	0.0
N–18	2	0.2	0.3	0.0	0.4	0.0
	4	1.5	0.1	0.0	0.9	1.4
	6	2.7	1.7	0.0	1.1	1.0
	8	2.7	1.9	0.0	1.1	0.8
	10	2.7	2.4	0.0	1.2	0.3
	13	2.7	2.0	0.0	2.4	0.7
	17	2.7	2.2	0.0	2.4	0.5
	20	2.7	2.6	0.0	2.2	0.1
N–22	2	0.5	0.2	0.1	0.4	0.2
	4	1.7	0.1	0.2	0.9	1.4
	6	2.0	1.5	0.0	1.3	0.5
	8	2.0	1.7	0.0	1.5	0.3
	10	2.1	1.6	0.1	1.5	0.4
	13	2.1	1.2	0.0	2.8	0.9
	17	2.1	2.0	0.0	2.8	0.1
	20	2.1	1.8	0.0	3.0	0.3

Culture number.	Days.	Nitrogen—parts per 100,000				
		Nitrates, total reduction.	Nitrites from nitrates.	Ammonia from		Undetermined nitrogen from nitrates.
				nitrates.	peptone.	
1.	2.	3.	4.	5.	6.	7.
N-23	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.2	0.0
	6	0.0	0.0	0.0	0.2	0.0
	8	0.0	0.0	0.0	0.2	0.0
	10	0.0	0.0	0.0	0.3	0.0
	13	0.0	0.0	0.0	0.4	0.0
	17	0.0	0.0	0.0	0.3	0.0
	20	0.0	0.0	0.0	0.7	0.0
N-24	2	0.5	0.0	1.7	0.8	0.0
	4	0.5	0.0	1.3	1.5	0.0
	6	0.5	0.0	1.7	2.2	0.0
	10	0.5	0.0	1.7	3.7	0.0
	13	2.5	0.1	2.6	4.2	0.0
	17	4.5	1.8	3.8	4.8	0.0
N-26	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.1	0.0
	6	0.0	0.0	0.0	0.2	0.0
	10	0.0	0.0	0.3	0.2	0.0
	13	0.0	0.0	0.3	0.1	0.0
	17	0.0	0.1	0.5	0.2	0.0
N-29	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.1	0.0	0.0
	6	0.0	0.5	0.0	0.8	0.0
	10	0.0	1.8	0.0	1.6	0.0
	13	1.5	4.8	0.0	1.9	0.0
	17	1.5	4.5	0.0	2.7	0.0
N-31	2	2.0	2.6	0.5	0.6	0.0
	4	2.5	4.0	0.5	1.1	0.0
	6	9.0	9.0	1.0	1.5	0.0
	10	9.0	13.0	1.0	1.6	0.0
	13	9.0	7.0	1.4	2.1	0.6
	17	11.0	15.0	1.5	2.4	0.0
N-33	2	0.0	0.0	0.0	0.0	0.0
	4	0.0	0.0	0.0	0.0	0.0
	6	0.0	0.0	0.0	0.0	0.0
	10	1.5	0.0	0.0	0.0	1.5
	13	1.5	0.1	0.1	0.0	1.3
	17	1.5	0.5	0.6	0.0	0.4

Culture number.	Days.	Nitrogen—parts per 100,000. Nitrates, total reduction.	Nitrites from nitrates.	Ammonia from nitrates.	Ammonia from peptone.	Undetermined nitrogen from nitrates.
1.	2.	3.	4.	5.	6.	7
N–38	2	0.0	0.0	0.0	0.1	0.0
	4	0.0	0.0	0.0	0.1	0.0
	6	0.0	0.0	0.0	0.4	0.0
	10	0.0	0.3	0.2	0.4	0.0
	13	0.5	0.7	0.1	0.4	0.0
	17	0.0	0.9	0.7	0.4	0.0
N–40	2	0.0	0.8	0.0	0.6	0.0
	4	2.5	1.6	0.0	1.0	0.9
	6	2.5	2.0	0.1	1.1	0.4
	10	2.5	2.4	0.2	1.3	0.0
	13	2.5	1.8	0.2	1.4	0.5
	17	2.5	2.2	0.4	1.5	0.0
N–41	2	0.5	1.5	0.0	0.5	0.0
	4	2.5	2.4	0.0	0.8	0.1
	6	2.5	3.2	0.0	1.0	0.0
	10	2.5	3.5	0.5	1.0	0.0
	13	2.5	5.5	0.4	1.1	0.0
	17	2.5	4.0	0.3	1.8	0.0

Gain or Loss of Nitrogen.—On all the cultures which were studied, besides the daily tests for nitrates, nitrites and ammonia, tests were made for total organic nitrogen in the solutions by the Kjeldahl method at the beginning and end of the period of incubation. By the use of these Kjeldahl values, together with the values for ammonia, nitrites and nitrates, assuming that none of the nitrogen is present in forms which would not be determined by these methods, we have been able to compute the gain or loss of nitrogen in the solutions, and to compare the reduction of organic nitrogen with the reduction of nitric nitrogen.

Of the results obtained with thirty cultures which are included in Table III, eighteen of the cultures showed a loss of nitrogen in the peptone solution and twelve of the cultures showed a gain. In the solution containing nitrates sixteen of the cultures showed a loss of nitrogen and thirteen showed a gain. Nineteen of the cultures agreed as to gain or loss of nitrogen as determined in the two solutions, one of the cultures showed no change in the nitrate solution, and ten of the cultures showed a gain or loss in the peptone solution when the reverse was true in the nitrate solution. With seven of these ten cultures, the gain or loss of nitrogen in one

solution or the other was less than 0.5 part per 100,000 of nitrogen, this being the limit of error of the Kjeldahl method as determined by duplicate analyses of all the cultures. One culture showed a gain or loss of exactly 0.5 per cent. and this may be included with the other seven, leaving only two cultures in which there was an appreciable discrepancy in the two solutions, these being culture No. 9, which showed a gain of 1.2 parts in the peptone solution and a loss of 1.8 parts in the nitrate solution, and culture No. 34, which showed a loss of 1.7 parts in the peptone solution and a gain of 12.1 parts in the nitrate solution. The maximum gain in nitrogen in the peptone solution was made by culture No. 10, which gained 12 parts nitrogen, and the maximum gain in the nitrate solution was by culture No. 34, which gained 12.1 parts nitrogen. The greatest losses were made by culture No. 16, which lost 5 parts of nitrogen in the peptone solution, and by culture No. 32, which lost 6.6 parts of nitrogen in the nitrate solution. Assuming that the error of the methods is 0.5 part per 100,000, twenty-two of the thirty cultures gained or lost more than this amount in the peptone solution, and twenty-three gained or lost more than this amount in the nitrate solution. Comparing the reduction of organic nitrogen by the same cultures in the two solutions, with twenty cultures, a greater reduction occurred in the nitrate solution than in the peptone solution, either through increased activity of the bacteria in the presence of nitrates, or through secondary reactions between the decomposition products of the nitrates and organic matter. With seven of the cultures the reduction of organic nitrogen in the nitrate solution was less than in the peptone solution, and this may possibly be ascribed to the slight deterrent action of nitrates on certain cultures which has been mentioned before. Of the cultures which gained nitrogen in the nitrate solution nine were able to reduce nitrates and four did not reduce nitrates, while of the cultures which showed a loss of total nitrogen in the nitrate solution eleven reduced nitrates and five did not.

Comparing the reduction of organic nitrogen in the nitrate solution with the reduction of nitric nitrogen we find that of the twenty-four cultures which showed a reduction of organic nitrogen of 0.5 part or more, seven failed to reduce nitrates, while of the six cultures which did not cause any material reduction in the organic nitrogen three were able to produce a decided re-

duction of the nitric nitrogen. The figures showing the reduction of organic nitrogen and the reduction of nitric nitrogen, together with the amount of nitrogen determined by the various methods and the probable gain or loss in the nitrogen content of the solutions, are shown in the following table:

TABLE III.—SHOWING THE GAIN OR LOSS OF NITROGEN AS COMPUTED FROM KJELDAHL VALUES AND DETERMINATIONS OF NITRATES, NITRITES AND AMMONIA.

	Peptone solution.			Nitrate solution.				
Culture.	Reduction of organic nitrogen.	Determined as ammonia.	+ = Gain. − = Loss.	Reduction of organic nitrogen.	Reduction of nitric nitrogen.	Total reduction of *Initial* nitrogen.	Determined as nitrites and ammonia.	+ = Gain. − = Loss.
	Parts per 100,000.							
1	1.6	2.1	+0.5	2.2	0.0	2.2	3.9	+1.7
2	2.4	1.1	—1.3	0.0	0.0	0.0	1.0	+1.0
4	0.0	0.6	+0.6	4.5	6.0	10.5	12.5	+2.0
6	6.8	1.8	—5.0	0.0	1.0	1.0	0.9	—0.1
7	4.5	2.2	—2.3	3.2	3.5	6.7	3.4	—3.3
8	0.0	2.3	+2.3	0.0	2.6	2.6	3.1	+0.5
9	1.1	2.3	+1.2	2.8	5.3	8.1	6.8	—1.3
10	6.0	18.0	+12.0	8.3	2.7	11.0	12.0	+1.0
11	0.1	0.5	+0.4	4.5	6.0	10.5	7.8	—2.7
12	2.1	3.8	+1.7	2.3	0.0	2.3	1.9	—0.4
13	3.3	4.2	+0.9	1.4	0.0	1.4	1.4	0.0
16	3.5	7.5	+4.0	0.4	0.0	0.4	1.0	+0.6
17	3.0	0.2	—2.8	3.0	2.3	5.3	5.2	—0.1
18	1.8	2.2	+0.4	2.4	2.7	5.1	4.4	—0.7
22	3.1	3.0	—0.1	2.3	2.1	4.4	4.4	—0.0
23	0.0	0.7	+0.7	0.1	0.0	0.1	0.5	+0.4
24	6.2	4.8	—1.4	8.4	4.5	12.9	10.4	—2.5
25	0.5	0.3	—0.2	4.9	9.0	13.9	17.7	+3.8
26	0.4	0.2	—0.2	1.6	0.0	1.6	0.8	—0.8
27	1.5	0.9	—0.6	2.5	0.0	2.5	0.6	—1.9
29	2.3	2.7	+0.4	3.2	1.5	4.7	6.4	+1.7
30	0.5	0.3	—0.2	0.0	2.5	2.5	4.7	+2.2
31	3.2	2.4	—0.8	5.5	11.0	16.5	18.9	+2.4
32	5.3	4.8	—0.5	9.0	1.5	10.5	3.9	—6.6
33	2.0	0.0	—2.0	2.2	1.5	3.7	1.1	—2.6
34	1.7	0.0	—1.7	4.1	2.5	6.6	18.7	+12.1
36	1.1	0.4	—0.7	1.5	0.0	1.5	0.6	—0.9
38	0.6	0.4	—0.2	2.1	0.0	2.1	2.0	—0.1
40	2.9	1.5	—1.4	2.8	2.5	5.3	4.1	—1.2
41	2.3	1.8	—0.5	3.1	2.5	5.6	6.1	+0.5

The Distribution of Ammonifying and Denitrifying Bacteria in Sewage and Effluents from Sewage Filters, and the Relation of Peptonization to Other Biochemical Functions.—Of the biochemical functions of bacteria concerned in sewage disposal the most important and the ones which can be most accurately determined are the power to liquefy insoluble organic matter, and the power to break down the soluble proteids, peptones, albumoses, etc., into ammonia. These two reactions are the first essentials, and are closely seconded in importance by those reactions by which this ammonia is converted into some stable product such as nitrates, in which form it is at least inoffensive. Denitrification, while in a measure a retrograde process, undoubtedly does occur to a greater or less extent in all biological methods of sewage treatment, and it is an open question whether the secondary reactions between the reduction products of the nitrates and the intermediate products of peptonization are not of more importance and more worthy of careful study and control than has generally been thought to be the case. While these changes may be purely chemical in their nature, or may be due to the action of enzymes, they are brought about directly or indirectly by the action of bacteria, and for this reason some figures as to the relative numbers of bacteria in sewage and in the effluents from some of the various types of sewage filters, may properly be inserted in a paper of this kind.

During a study of the biochemical functions of the bacteria concerned in sewage purification, previously reported, determinations of the ammonifying and denitrifying powers of over 300 cultures of bacteria were made, and in addition, tests were made for the amount of liquefaction which many of these cultures were able to produce in gelatin. The solutions and methods of procedure for the nitrogen tests were the same as previously described in this paper, a standard period of incubation of seven days at 20° C. being employed. The method of making the quantitative gelatin tests was as follows: Test-tubes of a uniform bore of ten millimeters were filled to a depth of 100 millimeters with standard beef peptone gelatin, and the entire surface of the gelatin was inoculated with the culture. Any liquefaction which occurs must proceed straight down from the surface of the gelatin, and the depth of this liquefaction in millimeters, in a given time is a numerical measure of the rate or amount of liquefaction.

The cultures were selected from the colonies on the gelatin plates in such a way as to represent as closely as possible all of the kinds of bacteria in the samples, that is, all of the kinds of bacteria which would be shown by the ordinary plate method. From the data thus accumulated, it has been possible to compute the percentage of the total number of bacteria in the individual samples which possessed these functions, and by averaging the percentages in the various samples to determine approximately the percentage of the total bacteria in samples of different kinds which were able to produce ammonia in peptone solution and to reduce nitrates. From these figures it appears that a considerable majority of the bacteria in sewage and in the effluents and material from sewage filters are possessors of both of these functions. The results are shown in the following table:

TABLE IV.—SHOWING PERCENTAGE OF AMMONIFYING AND DENITRIFYING BACTERIA IN SEWAGE AND THE EFFLUENTS FROM SEWAGE FILTERS.

Source.	Number of samples.	Percentage of total bacteria which ammonify peptone.	Percentage of total bacteria which reduce nitrates.
Sewage	3	90	70
Septic sewage	6	56	59
Effluent contact filters	3	60	61
Effluent trickling filters	4	59	71
Effluent sand filters	15	70	70
Sand from sewage filters	3	90	70

The tests for gelatin liquefaction were made on 157 of the before-mentioned cultures and a comparison of the results of these tests with the various changes in the nitrogen content of the test solutions enables us to trace, in a general way, the relation between the peptonizing power as represented by the amount of liquefaction of gelatin and the denitrifying and ammonifying powers. These results have been grouped in Table V, according to their liquefying power. Comparing the results obtained with cultures which liquefied with those which did not liquefy we find that the liquefiers have an average ammonifying power nearly twice as great as the non-liquefiers and that they have a denitrifying power about three times as great. In each group of cultures, both liquefying and non-liquefying, we find some which cause large changes in the nitrogen content and others which cause no change whatever. A study of the individual analyses reveals, however, that

while 30 per cent. of the non-liquefiers were unable to reduce nitrates, only 8 per cent. of the liquefying cultures failed in that function. Again, 32 per cent. of the non-liquefying cultures did not produce nitrites in the nitrate solution and the same percentage of cultures failed to show any ammonia production in the peptone solution. On the other hand, the number of cultures which failed to produce nitrites was 15 per cent. or less than one-half as many, and the percentage of cultures which failed to break down peptone into ammonia was only 2 per cent., or one-eighth as many as in the case of the non-liquefying cultures. In other words, as shown by the amount of change and by the percentage of cultures reacting, the liquefying cultures are much more active in causing changes in the form of the nitrogenous ingredients of the solution than are the non-liquefying cultures. The figures showing the average amount of nitrogen lost from nitrates which was not determined as nitrites or ammonia, also appear to follow the same rule as above stated, although the results are of doubtful significance for reasons which have been previously discussed. Comparing the relative liquefying power with the other functions, we find that as this power increases the power to reduce nitrates also steadily increases. The relation between the increase in the liquefying power and the nitrite production and the ammonification of peptone, however, is less marked. It is probable however, that with a more extended study covering a larger number of cultures the ratio between these functions would be more uniform.

CONCLUSIONS.

With the advent of the various biological methods of sewage disposal in which the activity of various classes of bacteria have to be carefully controlled in order to accomplish the desired end, a knowledge of the various biochemical reactions taking place and the bacteria which produce these changes becomes necessary. Of the various changes occurring in the sewage during treatment, the main problem is to change the nitrogenous matter from a highly objectionable form in which it is present into a non-putrescible and inoffensive form, since in the process of changing the form of the nitrogen content the carbonaceous matter is also converted into simple elementary compounds. Consequently, the problem narrows down to a study of the bacteria causing changes in the nitrogenous matter, and since the study

TABLE V.—SHOWING RELATION BETWEEN LIQUEFYING POWER AND DENTIRIFYING AND AMMONIFYING POWER.

	Cultures which did not liquefy gelatin.	Cultures which liquefy gelatin.	Liquefying power between 1 and 10.	Liquefying power between 11 and 20.	Liquefying power between 21 and 30.	Liquefying power between 31 and 40.	Liquefying power between 41 and 50.
Average liquefaction.	. .	. .	6.	15.	24.	35.	49.
Nitrate reduction, average	1.8	5.3	3.1	5.2	6.2	6.8	6.9
" " maximum	7.0	9.6	8.7	9.3	9.3	..	9.6
" " minimum	0.0	0.0	0.0	0.0	0.0	..	2.0
Per cent. of cultures did not reduce nitrates	30.0	8.0	29.0	3.0	20.0	..	0.0
Nitrite production, average	1.6	6.1	3.5	6.5	7.7	0.0	6.5
" " maximum	11.0	12.0	11.0	12.0	11.0	..	11.0
" " minimum	0.0	0.0	0.0	0.0	0.0	..	0.0
Per cent. of cultures did not produce nitrites	32.0	15.0	35.0	8.0	20.0	..	14.0
Ammonification of peptone, average	0.4	0.7	1.1	1.8	1.4	0.6	1.4
" " " maximum	1.9	5.2	3.2	5.2	2.1	..	4.5
" " " minimum	0.0	0.0	0.0	0.0	0.0	..	0.1
Per cent. of cultures did not produce ammonia from peptone	32.0	2.0	6.0	0.0	10.0	..	0.0
Reduced nitric nitrogen not determined as nitrites and ammonia, average	0.7	1.2	0.3	0.2	0.1	5.3	1.1
maximum	4.6	5.6	2.4	1.8	0.8	..	5.6
minimum	0.0	0.0	0.0	0.0	0.0	..	0.0
Per cent. of cultures which did not show undeterminable nitrogen	59.0	45.0	76.0	27.0	80.0	..	62.0
Number of cultures	44.	113.	17.	64.	10.	1.	21.

of these bacteria under natural conditions, *i. e.*, in the sewage and in the filters, surrounded, as they are, by other types of bacteria and under conditions which are constantly changing, is beset with difficulties, it becomes necessary to study these bacteria in pure culture and under constant conditions, in order to acquire data sufficiently exact to be used in an analysis of the more complex problems which occur in actual practice. The present paper is a portion of a more extended investigation into the types of bacteria normally present in sewage and the effluents of sewage disposal systems, and their rôle in the causation of the biochemical reactions occurring during the processes of treatment, and has to deal with the specific changes which representative types of bacteria in pure culture may produce in solutions containing nitrogen in forms more or less common in sewage during its purification. Thirty cultures of bacteria, common in sewage and the effluents from sewage filters, have been studied carefully to determine the character and amount of change brought about by their action on peptone and nitrates.

From the results obtained in this study it becomes possible to state definitely that bacteria, common in sewage purification, are able to produce ammonia from organic matter, to reduce nitrates to nitrites, to ammonia and probably to elementary nitrogen, to liberate nitrogen from solutions of organic matter either with or without the presence of nitrates or its reduction products, and also to fix atmospheric nitrogen under the same conditions, all of which reactions have been noted by other observers, but about which there has been more or less controversy. Many sewage bacteria probably also produce the lower oxides of nitrogen as reduction products of nitrates, which oxides may play an important part in the further decomposition of the organic matter in solution, either through catalytic action or by direct chemical reaction. Furthermore, certain of these bacteria may produce an oxide or at least a compound of nitrogen intermediate between nitrates and nitrites, which has apparently not been noted hitherto. The amount of ammonia produced by the different cultures has ranged from 0 to 18 parts per 100,000, and the rate of ammonification has varied considerably, some of the cultures reacting as early as the fourth day, while other cultures, which eventually reacted strongly, did not begin to ammonify until after periods of ten to fourteen days. Similar phenomena have been

noted with regard to the reaction of the cultures on nitrates. Some have reduced the nitrates rapidly and completely, some have denitrified slowly, some have reacted only after a considerable time of incubation, and others have caused no change. The character of the reduction products, both as regards amount and rate of formation has also been interesting. Some cultures have been able to reduce the nitrates to nitrites, ammonia and elementary nitrogen continuously from the start, while with other cultures the reduction to these various bodies has occurred consecutively, and with still others one or another of the reduction products has not occurred during the period over which the examination of the cultures extended. In a few instances nitrites have been produced in quantities far greater than the amount of nitrates, and if the results are not in error, this can be explained only on the supposition that a direct oxidation or nitrification has occurred, caused either by direct bacterial action or by some undetermined secondary reaction.

Regarding the distribution of ammonifying and denitrifying bacteria in sewage and the effluents from sewage filters, based on a study of the biochemical functions of over 300 representative cultures from a variety of samples, it may be said that a majority of the bacteria from these sources, which are determinable by the ordinary plate methods, using gelatin as a culture medium, reduce nitrates and decompose peptone into ammonia, although these two functions are not always correlated with the same species. By the use of quantitative tests for the amount of liquefaction produced in gelatin by over 150 of these cultures, we have been able to determine approximately the relation between the peptonizing power or power to liquefy insoluble organic matter, and the ammonifying and denitrifying powers of sewage bacteria. We find that while many non-liquefying bacteria are able to reduce nitrates, or to ammonify peptone or to do both, and many liquefying bacteria do not possess these functions, nevertheless, in a large majority of cases the possession of the first function means possession of one, and usually both of of the last two functions, and the average amount of change produced in the nitrogenous matter in solution is much greater with peptonizing bacteria than with those which are unable to liquefy gelatin. Furthermore, an increase in the liquefying power ap-

pears as a rule to be synonymous with increased ability to reduce nitrates and to ammonify peptone.

In the present paper we have dealt with the reactions produced by pure cultures of bacteria, it being necessary that these elementary reactions should be thoroughly understood before we attempt the study of mixed cultures, with the complicated series of secondary reactions which may occur between the reduction products of the different species. A practical application of the quantitative tests for the biochemical functions of various species combined with the numbers of bacteria of those species present in water and sewage has already been made, and the field is one which promises to bear fruit in the near future in a better understanding of the biological processes occurring in sewage treatment and in the more scientific control of the conditions which govern those processes.

LAWRENCE, MASS.

ON THE SPECIFIC ROTATION OF SALTS OF CASEIN.

BY J. H. LONG.

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IN THE literature there are a few references to the optical rotation of "casein" in solutions of weak alkalies, acids or neutral salts, but most of them refer to the old work of Hoppe-Seyler on products of doubtful purity,[1] or to later work by Béchamp with mixtures of somewhat uncertain composition.

Casein, as the term is now understood, is a nucleoalbumin of marked acid character, which exists in milk in the form of a calcium salt mixed or combined with phosphate. This combination may be easily broken up by addition of weak acids, especially acetic, yielding the pure substance, which seems to be quite insoluble in water, but readily soluble in alkali solutions with formation of acid or neutral salts. Like many of the proteins, this casein holds certain groups which impart to it a basic character by reason of which it combines, to a certain extent, with weak acids, forming another class of salts, but in this short paper the alkali combinations only are considered. Some of these alkali combinations have some commercial importance; nutrose and plasmon are essentially impure sodium salts.

[1] For literature see "Optical Rotation of Organic Substances," Landolt, Long's translation, p. 728, and Hoppe-Seyler's Handbuch der Phys. und Path. Chem. Anal., 6th ed., p. 259.

In the preparation of the casein employed in the present work about 5 liters of well skimmed milk were treated according to the general Hammarsten method. This milk had been run twice through the centrifugal separation process, the second run being made at high speed, especially for my work; but a minute trace of fat was left. To obtain the casein the milk was diluted with four or five volumes of water and treated with just enough dilute acetic acid to produce the maximum precipitation. The precipitate was allowed to settle and was then washed repeatedly by decantation with distilled water and finally dissolved in the requisite amount of weak sodium hydroxide, using phenolphthalein to show neutrality. This salt was again decomposed by weak acetic acid as before, and all the operations repeated several times. Finally the moist precipitate from the last acid treatment was drained on a Buchner funnel, washed with strong alcohol and with 2 liters of ether to remove the last traces of fat. The residue soon dried to a fine white, very light powder, which, after standing a week over strong sulphuric acid, was ready for use. It still held about 4 per cent. of water, which was determined by drying a small portion in the air-oven at 105°-110°. It contained about 0.6 per cent. of ash, as found by slow incineration at the lowest possible temperature.

To dissolve 5 grams (5.2 grams as used) of the powder 45 cc. of N/10 alkali are required to produce a solution neutral to phenolphthalein, but the 5 grams will dissolve completely in just one-half this alkali, or 22.5 cc., yielding when diluted to 100 cc. a practically clear liquid, which may be easily polarized in a 100 mm. tube. There is, in all cases, a slight opalescence, which makes it necessary to employ a brighter field than is usually required. A good light must therefore be employed. It is also necessary to work with a rather large half-shadow angle, which diminishes somewhat the delicacy of the reading. The following individual determinations were made, all at 20°.

Sodium Compound.—Five grams of casein +45 cc. of N/10 sodium hydroxide made up with water to 100 cc. The observed angle of rotation, α, in the 100 mm. tube was —5.175°, from which we have, based on the casein weight,

$$(\alpha)_D = -103.5°.$$

This is the product as made neutral to phenolphthalein. As mentioned above, a clear solution may be obtained with half

the alkali here used. For the salt formed with 5 grams of casein and 22.5 cc. of N/10 sodium hydroxide in 100 cc. I found $\alpha = -4.76°$ from which

$$(\alpha)_D = -95.2°.$$

The effect of presence of increased amounts of alkali was found by making solutions with 67.5 of N/10 alkali and 45 cc. of N/5 alkali and water to 100 cc., for the first of these I found $\alpha = -5.38°$, or

$$(\alpha)_D = -107.6°,$$

and for the second $\alpha = -5.59°$, or

$$(\alpha)_D = -111.8°.$$

This alkali may all be present in salt form, as will be pointed out in a paper to follow in which observations in another direction will be recorded.

Potassium Compound.—One solution was examined. This contained 5 grams of casein and 45 cc. of N/10 alkali with water to 100 cc. for the angle of rotation I found $\alpha = -5.22°$, or

$$(\alpha)_D = -104.4°.$$

Lithium Compound.—To prepare this I made first pure lithium carbonate from the best commercial carbonate. This contained neither sulphate nor chloride. A few grams of the thoroughly washed preparation were suspended in water and converted into the more soluble bicarbonate by a stream of carbon dioxide. The normal carbonate precipitated from this by heat was made up to a solution approximately N/10 and used to dissolve casein as were the hydroxides above. The first salt was made by dissolving 5 grams of casein in the equivalent of 22.5 cc. of N/10 LiOH solution. For this I found $\alpha = -4.74°$, with

$$(\alpha)_D = -94.8°.$$

The solution was acid to phenolphthalein. A solution, neutral to the indicator, was made by using just twice as much lithium carbonate. For this I found $\alpha = -5.04$, or

$$(\alpha)_D = -100.8°.$$

Ammonium Compound.—An ammonium salt was made with 45 cc. of N/10 NH_4OH, 5 grams of casein and water to 100 cc. The polarization gave $\alpha = -4.89°$, or

$$(\alpha)_D = -97.8.$$

In all these cases the specific rotation, based on the casein

present, is increased with increase of alkali. The values obtained are higher than the few given in the literature, but may be easily duplicated by other preparations from cows' milk. According to Béchamp[1] casein is slightly soluble in water; from such a solution he obtained a rotation $(\alpha)_j = -117.7°$, which is equivalent to about $(\alpha)_D = -105°$. This is practically the same as for the salts, as above described. The property is a constant, which may be utilized in the comparison of milks of different origin. Some experiments with human milk and the milk of the goat are now in progress.

NORTHWESTERN UNIV., CHICAGO,
March, 1905.

THE EFFECT OF RUST ON THE STRAW AND GRAIN OF WHEAT.

BY FRANK T. SHUTT.

Received January 9, 1905.

THE prevalence of rust this season in certain districts of Manitoba led to many inquiries regarding the general effect of this fungus upon the wheat plant—both straw and grain—and more particularly as to how it might influence their feeding value. The importance of the subject made it desirable to obtain data on these points and accordingly samples of both rusted and rust-free wheat were obtained and analyzed.[2]

In order that the results should be strictly comparable, it was essential in procuring these samples that the clean and the affected wheat be of the same age and grown on the same soil. We were able to secure such specimens, both wheats being collected by hand on the same day in the same field on the farm of Sir Wm. Van Horne, at East Selkirk, Manitoba.

There was a marked difference in appearance between them, both in straw and grain. The rust-free wheat had a clear, bright yellow, a well-ripened straw, a normal ear, both as to size and color, and a plump, well-filled grain. On the other hand, the rusted wheat straw presented in general a dirty greenish brown appearance, and on closer inspection showed many spots or

[1] *Bull. Soc. chim.* [3], **4**, 18; **11**, p. 152. *Ber. d. chem. Ges.*, 1890, III, 741.

[2] Mention should be made that certain analyses of "rusted and frosted" wheat (grain) were made at the Minnesota Experiment Station in 1889, by Dr. Harper. From the results Dr. Harper concluded that the grain of such wheat was abnormal, both chemically and physically, and was about 2 per cent. richer in protein than "graded" wheat.

patches of infection, while its ears were smaller than normal and the kernels light and much shriveled.

ANALYSIS OF RUSTED AND RUST-FREE WHEAT, STRAW AND GRAIN.

	Weight of 100 kernels. Grams.	Moisture.	Crude protein.	Crude fat.	Carbohydrates.	Fiber.	Ash.
Straw from rust-free wheat.....	....	7.92	2.44	1.65	39.00	39.95	9.04
Straw from rusted wheat.....	....	7.92	7.69	1.97	38.44	36.78	7.20
Grain from rust-free wheat.....	3.0504	12.26	10.50	2.56	70.55	2.29	1.84
Grain from rusted wheat.....	1.4944	10.66	13.69	2.35	68.03	3.03	2.24

The Straw.—We first notice that in crude protein the rusted straw is much the richer. Under the term crude protein is included all those nitrogenous compounds of a food that go to repair and build up muscle and tissue. It may safely be concluded, therefore, that the rusted straw, containing, as it does, more than three times the protein found in the rust-free straw, is very much superior in feeding value.

Further, in the rusted straw we have a slightly higher percentage of fat—the constituent next in value to protein—and somewhat less fiber—the element of least value in a fodder—and hence there is additional evidence of the most satisfactory character to support the statement respecting the more nutritious nature of the rust-affected straw.

The Grain.—The small and shriveled character of the grain from the rusted wheat may be deduced from the data in the first column of the table—the weight of 100 kernels being only one-half that of 100 kernels from the unaffected wheat. This fact, however, from the standpoint of a feed, does not betoken a lessening of its nutritive qualities; indeed, as the data from the protein show, it has, weight for weight, considerably the higher value.

The protein of the shriveled grain is 3.19 per cent. higher than that of the plump grains from the rust-free plant. Part of this higher protein content in the smaller grain is no doubt to be accounted for in its larger proportion of bran—but it is due chiefly to

the fact that the transference and accumulation of starch in the kernel has been but partial and incomplete.[1]

Other features of note in the analysis of the grain from the rusted wheat are: (1) the somewhat larger percentages of fiber and ash—indicating more bran—and, (2) the lower water, carbohydrates and fat content.

Apart from the valuable information that these data furnish regarding the relative feeding value of the straw and grain of rusted wheat, we have in these results interesting evidence as to the physiological effect of the rust on the wheat plant. Speaking broadly, there are (after germination) two periods in the life of the wheat plant—the first, a period of feeding and assimilation; the second, a later and usually shorter period, during which the food materials accumulated in stem and leaf (straw) are transferred to and stored in the seed (kernel). There is, of course, no exact time when it can be said that the one ends and the other begins. Under normal conditions there is a gradual cessation of feeding, both by root and leaf, accompanied by an ever-increasing movement of the accumulated material to the seed. The first period is characterized by growth, the second is recognized by the maturation or ripening of the seed.

Further, it would seem that in the development of the seed, the albuminoids or protein are first transferred and later, towards the close of the maturation period, the carbohydrates (starch, etc.) are more particularly deposited.

The rust apparently does not affect the vitality of the wheat plant during the first stage or period, but as the season progresses and the ripening period advances the fungus attains the ascendency, crippling the energies and functions of the tissues and checking the movement of the food materials to the seed. In other words, the growth of the rust arrests development and induces premature ripening, which, as we have seen, means a straw in which still remains the elaborated food, and a grain containing less water, rich in protein and deficient in starch, and in appearance, small and shriveled.

It may be well to point out that although the rust makes the

[1] NOTE.—Some years ago in determining the relative feeding-value of frosted wheat (which presents a shriveled appearance very similar to that of the grain from rusted wheat), we found that the protein content was considerably higher than in the unfrosted, mature grain. It is evident that the effect of rust and frost, in this respect, is the same, resulting in a premature ripening, or rather a drying-out of the grain, which, as we have seen, means a kernel high in protein, but low in starch.

grain more nitrogenous, it at the same time very materially reduces the yield per acre, the present figures indicating a loss in weight of about 50 per cent.

We have not as yet been able to complete the analysis of the milling products of this shriveled wheat, but we may rest assur d until such time as the data are available that the proportion of bran to flour will be higher than from normally ripened wheat. We may, further, conjecture that this bran will be found slightly more nitrogenous than that from rust-free wheat. It is held by certain millers that the rust makes flour somewhat "stronger," but at the moment there are no data, I believe, to support this contention. The probabilities, from deduction, rather point to a deterioration or lack of "strength" in the gluten.

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OTTAWA, CANADA.

THE PREPARATION AND NITRATION OF METETHYLTOLUENE.

BY EDWARD BARTOW AND A. W. SELLARDS.

Received January 23, 1905.

WHILE the three possible ethyltoluenes have been made synthetically, and their properties studied, comparatively few of their derivatives have been prepared. There are recorded some halogen,[1] some sulphonic acid,[2] some nitro[3] derivatives and one amino[4] derivative. On account of the greater difficulty in obtaining *m*-ethyltoluene, only one derivative, a sulphonic acid, is recorded.

Some work done by one of us with *m*-isocymene[5] suggested the possibility of similar work with *m*-ethyltoluene.[5] We have prepared the *m*-ethyltoluene and tried on it the action of nitric acid.

The preparation of *m*-ethyltoluene presents some difficulties. It is best prepared according to the Fittig synthesis. The most convenient starting-point is, of course, a halogen derivative of toluene and an ethyl haloid, rather than a halogen derivative

[1] *Ber. d. chem. Ges.*, **11**, 225 (1878); **19**, 3088 (1886); **28**, 2651 (1895).

[2] *Ibid.*, **19**, 3090 (1886); **28**, 2649 (1895); *Ann. Chem.* (Liebig) **146**, 85; **193**, 199.

[3] *Ber. d. chem. Ges.*, **7**, 1513 (1874); **19**, 3090; **27**, 2084 (1894); **28**, 2649 (1895); *Ann. Chem.* (Liebig), **136**, 314.

[4] *Ber. d. chem. Ges.*, **15**, 1650 (1882).

[5] Inaug. Diss., Göttingen (1895).

of ethylbenzene and a methyl haloid. For our ethyl haloid we used ethyl bromide. For the halogen derivative of toluene we used, in part, *m*-chlortoluene from Kahlbaum, and in part *m*-bromtoluene prepared in this laboratory.

The *m*-bromtoluene must be prepared indirectly, since by action of the halogens on toluene only ortho and para compounds result. We find that there are several methods for its preparation, but the best are the two following: In one benzaldehyde is nitrated, forming *m*-nitrobenzaldehyde; this is treated with phosphorus pentachloride, making *m*-nitrobenzalchloride; this, by reduction, gives *m*-toluidine; *m*-toluidine by diazotizing and treating according to the method of Sandmeyer gives *m*-bromtoluene.

The second method depends on the bromination of *p*-toluidine and the removal of the amino group from the product. We prepared our *m*-bromtoluene by the second method. Our method was practically like that recommended by Wroblewsky,[1] but we find that sodium hydroxide in concentrated aqueous solution will serve as well as potassium hydroxide for saponifying *m*-brom-*p*-acetoluidine (compare Grete).[2]

In the Griess reaction when nitrous acid is led into an alcoholic solution of the *m*-brom-*p*-toluidine, we also find that a thick crystal broth, not noted by Wroblewsky, is formed. These crystals were purified and investigated by Bartow and Allen[3] and found to have a composition and molecular weight corresponding to 2,2′-dibrom-4,4′-dimethyl diazoaminobenzene, $CH_3BrC_6H_3N_2$—$NHC_6H_3BrCH_3$ (melting-point, 111.4°-112.0°). These crystals were stable when the solution was neutral, and care was taken to cool the solution and the nitrous acid. A few drops of sulphuric acid causes almost immediate replacement of the amino group by hydrogen. The product, after washing with water, diluting with ether, and drying with calcium chloride, was used in the preparation of *m*-ethyltoluene by the Fittig synthesis.

PREPARATION OF *m*-ETHYLTOLUENE.

We used 30 per cent. more than the calculated amount of ethyl bromide, and 50 per cent. excess of sodium for a given amount of chlor- or bromtoluene. The reaction takes place with considerable violence, making it necessary to cool the re-

[1] *Ann. Chem.* (Liebig), **168**, 147.
[2] *Ibid.*, **177**, 231.
[3] *Trans. Kan. Acad. Sci.*, **19** (1905).

action mixture with salt and ice. Once the reaction miscarried, giving *m*-ditolyl. This result was prevented when the sodium, covered with ether, was thoroughly cooled and the mixture of ethyl bromide and chlor- or bromtoluene was added slowly, 2 to 3 cc. every thirty minutes.

In our first experiments, after driving off the ether on a water-bath, we distilled the hydrocarbon from the sodium bromide and the excess of sodium. On fractionating the distillate the temperature rose gradually from 120° to 170° with no larger amount distilling at 158°—the boiling-point of *m*-ethyltoluene. By repeated fractionations with a Linnemann dephlegmator we obtained about 4 grams, boiling at 158°, representing the yield from 25 grams of *m*-chlortoluene.

As we used the sodium and the ethyl bromide in large excess, we were at a loss to account for the small yield of *m*-ethyltoluene and for the large quantity of by-products formed. We thought it not unlikely that the high temperature required to distil the hydrocarbon from the excess of sodium, as well as the presence of metallic sodium, might tend to break down the ethyltoluene. We therefore attempted, by means of water, to destroy the blue compound and remove the excess of sodium by means of water, using a sufficient amount of ether to prevent any great rise in temperature. Accordingly, after the completion of the reaction and the formation of a blue compound, a considerable quantity of commercial ether was added to the mixture and a reversed condenser was connected to the flask containing the mixture. Then water was added drop by drop. The color quickly changed from blue to white, and as more water was added from time to time the sodium was dissolved. Though the ether was raised to boiling, no trouble was experienced in the removal of the sodium.[1]

When the sodium was used up the ethereal solution of the hydrocarbon and the water solution of sodium bromide were separated, and the former evaporated and fractionated. Without a dephlegmator 7 grams of *m*-ethyltoluene, boiling at 158°, were obtained. This represented the yield from 25 grams of *m*-chlor-

[1] Before carrying out the above experiment in the preparation of *m*-ethyltoluene, we tried with success the effect of the method in making ethylbenzene from brombenzene and ethyl bromide. Several students have since successfully applied this method for the removal of the excess of sodium. It is certainly much easier than the method recommended by Gattermann's "Praxis d. organ. Chem."

toluene, whereas only 4 grams were obtained when the hydrocarbon was distilled from the sodium.

The crude product thus obtained by means of water contains very few impurities. We have used it successfully in the preparation of nitro derivatives. We obtained better yields of ethyl toluene from bromtoluene than from chlortoluene.

NITRATION OF *m*-ETHYLTOLUENE.

Of the five known nitro ethyl toluenes two are derivatives of *o*-ethyltoluene and three of *p*-ethyltoluene. We have prepared two of the possible nitro derivatives of *m*-ethyltoluene, a dinitro and a trinitro derivative. Our attempts to isolate a mono-nitro derivative have not been successful.

Dinitro-m-ethyltoluene.—One part of *m*-ethyltoluene was slowly added, drop by drop, to seven parts of fuming nitric acid cooled by a freezing-mixture of salt and ice. After all the *m*-ethyltoluene was added the mixture was kept surrounded by ice water for fifteen hours, or until a test in water would sink completely. The whole reaction mixture was then poured into water. The oil which separated out was taken up with ether, washed free from acid, and the ethereal solution dried over calcium chloride. The ether was then evaporated and the residue placed in a vacuum over sulphuric acid. The product would not distil without decomposition, but could be distilled with steam. Analysis gave: C, 51.23; H, 5.03. Calculated for $C_9H_{10}O_4N_2$: C, 51.4; H, 4.8.

Reduction of the Dinitro-m-ethyltoluene.—By leading dry hydrochloric acid gas into a solution of dinitro-*m*-ethyltoluene in alcohol, containing the required amount of tin to reduce both nitro groups and then removing the tin with hydrogen sulphide, a diamine was obtained. We did not obtain enough for an analysis. A small amount with nitrous acid gave a compound analogous to Bismark-brown, indicating the meta position of the amino groups and hence of the nitro groups. There may be, however, a mixture of dinitro compounds.

S-Trinitro-m-ethyltoluene.—For the preparation of the trinitro derivative 1 part of *m*-ethyltoluene was added to 7 parts of fuming nitric acid in the same manner employed in making the dinitro compound. Without separating it from the nitric acid the mixture was poured into 15 parts of a mixture of equal volumes of fuming nitric and concentrated sulphuric acids. After

warming for an hour the whole mixture was poured on to cracked ice. A solid was obtained. After three crystallizations from absolute alcohol nearly colorless crystals were obtained, which melted at 86°.

Analysis gave: C, 42.63; H, 3.99. Calculated for $C_9H_9O_6N_3$: C, 42.3; H, 3.5.

Therefore, we conclude that the compound is 2,4,6-trinitro-3-ethyltoluene, because we would expect the three nitro groups to take the symmetrical position with reference to each other by direct nitration. Furthermore, we were able to obtain a crystalline compound when equal molecules of the substance and aniline were mixed in alcoholic solution.

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THE DECOMPOSITION OF AMMONIA AT HIGH TEMPERATURES.

BY ALFRED H. WHITE AND WM. MELVILLE.

Received January 14, 1905.

THE fact is well known that ammonia gas decomposes at a red heat into nitrogen and hydrogen, which recombine to only a very slight extent, if at all, on cooling. Deville and Troost[1] showed this very clearly. Ramsay and Young[2] in addition showed the very marked influence exerted by the character and extent of surface in contact with the gas, particularly at the higher temperatures. Their method of work was to pass dry ammonia gas through heated tubes of various materials and filled with various solid substances. Under circumstances to which some reference will be made later, decomposition became practically complete as the gas flowed through the hot tube. Recently Perman and Atkinson[3] have studied the decomposition of ammonia in a different manner. They used a porcelain globe placed in a constant temperature oven and keeping the volume constant, measured the decomposition by the increase in pressure. They found that at high temperatures, such as 1100° C., decomposition was practically complete in their apparatus in twenty minutes. They consider that the volume of the cold stem of their globe is suffi-

[1] *Compt. Rend.*, **56**, 895.
[2] *J. Chem. Soc.*, **45**, 88.
[3] *Proc. Roy. Soc.*, 1904, p. 110.

cient to account for the small trace of ammonia which escaped decomposition, and hold that there is no evidence of a state of equilibrium. They also note the effect of the nature of the contact surface in the markedly different action of an old and a new porcelain globe and the effect of platinizing the interior of the globe.

Practically, all the world's supply of ammonia comes from the destructive distillation of coal, mostly in retorts where it is exposed to the decomposing influence of the red-hot coke and the walls of the retort. Apparently, the decomposition is considerable, for it is calculated that only 12 to 14 per cent. of the nitrogen of the coal passes into the gas as ammonia, while from 25 to 30 per cent. gets into the gas as free nitrogen. There is no absolute proof that this free nitrogen is formed by the decomposition of the ammonia, but the fact that the yield of ammonia is four times as great in the Mond gas producer where the coal is subjected to distillation at a lower temperature and the products are diluted and rapidly swept out by a current of gas, gives considerable support to the theory that much ammonia is decomposed in the retorts of the gas works. Inasmuch, however, as illuminating gas contains nearly fifty times as much hydrogen as ammonia the presence of so large an amount of one of the decomposition products should, under the usual conditions of equilibrium, lessen the decomposition of the ammonia to a measurable degree. It might also be possible that equilibrium is already attained in ordinary practice in the manufacture of illuminating gas so that a longer stay of the gas in the retort would not further increase the decomposition of the ammonia. It was largely with a view to studying the technological points involved that the following experiments were undertaken to throw some light, if possible, on the question of the influence of change of temperature on decomposition, and also the effect of diluting the ammonia with one of the products of combustion and with other gases which are usually present in gas manufacture.

The following experiments were all made with one glass combustion tube and were terminated when the tube cracked in the attempt to investigate the effect of introducing a large amount of water vapor with the ammonia gas. In this apparatus were tested at various temperatures pure ammonia gas, and ammonia diluted with hydrogen, nitrogen, carbon monoxide and water

vapor. The ammonia gas was generated by dropping pure aqua ammonia on solid caustic soda and was dried by soda-lime. Its purity, as determined by absorption in acid, was 99.85 per cent. The dry ammonia was collected in a graduated 2-liter gas-holder, capable of being filled with dry mercury and provided with a manometer and an outlet stop-cock bearing a long sweep arm moving over a scale. By setting the stop-cock at a given point and carefully watching the pressure, the flow of gas could be kept approximately constant. A visual check on the rate of flow of gases was also afforded by a slightly inclined tube of mercury through which the gas bubbled. The combustion tube itself was of Jena glass of an internal diameter of 16 mm. At the exit end it was drawn down and fused to a glass tube of 6 mm. internal diameter in order to cool and convey the gases from the hot zone as rapidly as possible. A side-arm was fused on near the inlet end provided for the introduction of the gases. The LeChatelier pyrometer tube of glazed porcelain, 12 mm. in external diameter, passed through the open, large end of the tube. A gas-tight joint was assured by a layer of sealing-wax an inch thick, poured both into the annular space and around the platinum wires inside of the pyrometer tube. The bare thermocouple was left exposed to the gases and was about 25 mm. from the drawn-down portion of the combustion tube. The ammonia gas, therefore, passed through the annular space between the pyrometer tube and the combustion tube, and its temperature was measured just as it was leaving the large portion of the tube and was about to be rapidly withdrawn and cooled. The glass combustion tube was wrapped with asbestos and placed in an iron jacket in a combustion furnace provided with an automatic gas-pressure regulator. The glass tube was so placed that only about 200 mm. of its length was heated, and of this length about 25 mm. was of the 6 mm. tube and of 175 of the 16 mm. The plan was that the gases should pass through a uniformly heated tube for about 175 mm. to the constriction, then about 25 mm. more through the hot constricted tube to prevent the thermocouple from being chilled by the cold tube and then be quickly cooled down. An inspection of the tube, since it has been broken, shows that the result was as anticipated for the tube shows in just the portion planned, the milkiness characteristic of these tubes when heated for a long time to their softening-point. At the outlet of the combustion tube was a three-way cock, one tip of which

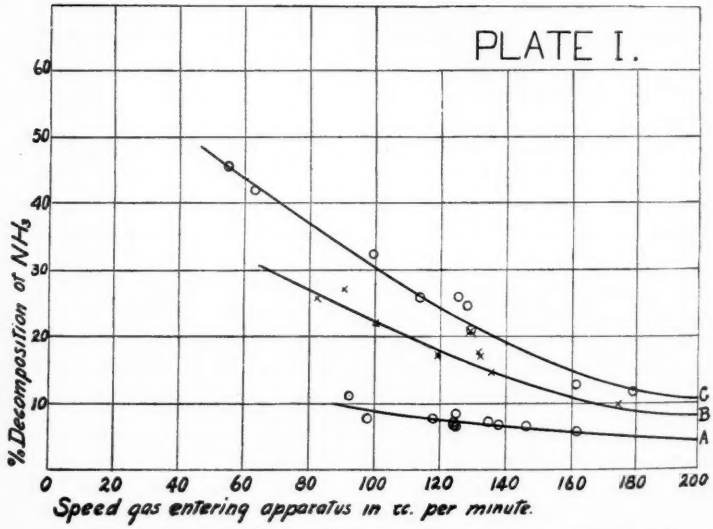
opened into the air and was used during the preliminary manipulations of each test. To the other tip was fused the nitrometer for collecting the gas. Fused glass joints were used wherever possible throughout the apparatus. In making an experiment the furnace was allowed to heat until the temperature had become stationary, and ammonia gas from the 2-liter gas-holder was run in, the rate being held constant, as far as possible, by keeping the pressure on the gas-holder constant, and the stop-cock open at a definite angle. About 0.5 liter was run in first to sweep out the train, the products passing through the final 3-way cock into the open air. Then by turning the 3-way cock the gases were passed into the nitrometer containing standard acid until the nitrometer was nearly filled with unabsorbed gas, the duration of the experiment being taken by a stop-watch. The amount of undecomposed ammonia was determined by titration of the standard acid, and the amount of ammonia decomposed from the volume and composition of the gases in the nitrometer. Since ammonia on decomposition gives three volumes of hydrogen to one of nitrogen this method allows the calculation of ammonia decomposition when either of the gases, hydrogen or nitrogen, has been mixed with the ammonia before decomposition. All gas analyses were made in duplicate with the burette for exact gas analysis, devised by one of us.[1] All data regarding per cent. of decomposition and rate of flow have been figured from the analysis of the contents of the nitrometer, the first graduated gas-holder being merely used to obtain an approximation of the conditions desired. Every result involves a determination of the temperature of the furnace, a titration for undecomposed ammonia, a measurement of the volume of the decomposed gases in the nitrometer, an analysis of them and a determination of the time required for their collection, usually considerably less than a minute. Since every result thus involves these five experimentally determined factors and an error in any one of which seriously affects the final figure, it is not strange that occasionally figures are obtained which are not in harmony with the majority.

Thirteen series of experiments are presented here, each one involving the measurement of decomposition of at least three temperatures. The temperatures aimed for were 600° C., which rep-

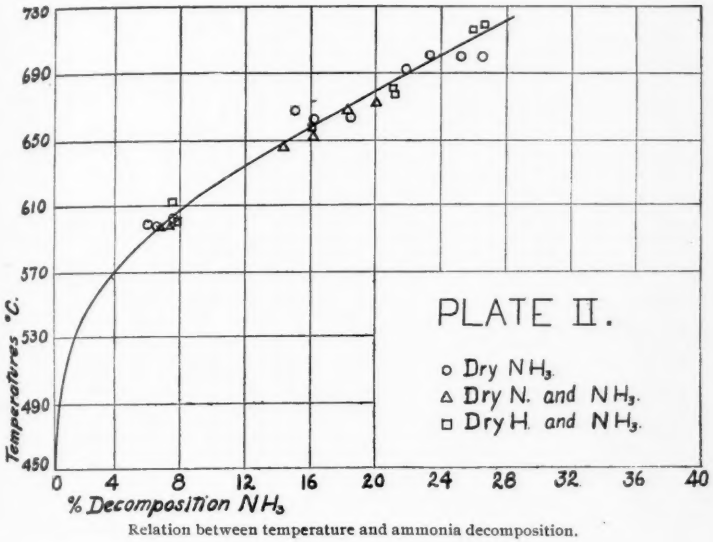
[1] This Journal, **22**, 343.

resented only a small decomposition, 690°, which was about the highest temperature which the furnace was certain to give, and an intermediate point of 650°. Owing to the difficulty of adjusting the furnace to exactly these points, the measurements were made whenever the furnace had reached a fairly constant temperature in the neighborhood of the point sought. Practically, all the temperatures come within 13° of the desired temperature. At first it was intended to keep the rate of flow of gases constant while varying the temperature. When it was found that this could not be done with sufficient accuracy wide variations were purposely introduced in the rate of flow to furnish the ground for the necessary correction. The three curves of Plate I show the relation between speed and decomposition, the number of cubic centimeters of gas entering the decomposition tube per minute being plotted as abscissae and the per cent. decomposition of the ammonia as ordinates. Curve A gives the results for the zone of temperature ranging from 587°-613°, and will be alluded to from its mean temperature as the curve at 600°. Similarly the mean temperature for Curve B is 650° and for Curve C 690°. Thirty-six points are thus plotted in the three curves, every point of all the experiments coming within the limits of temperature being represented irrespective of whether the gas was pure ammonia, or ammonia mixed with hydrogen, nitrogen, carbon monoxide or water vapor. The only results from all the series not included are those where water vapor and carbon monoxide are simultaneously present, which have been omitted because there is evidently a secondary reaction taking place. The numerical data from which Plate I was prepared are given in Tables I, II and III. Although the points, especially those with carbon monoxide, scatter somewhat there can be no mistaking the general directions of the three curves. The fact that the points range themselves on a curve at all shows very clearly that the nitrogen, hydrogen and carbon monoxide are acting almost completely as inert gases, for did the presence of its own volume of hydrogen or nitrogen have any influence further than dilution we would not find the same percentage of ammonia undergoing decomposition in the two cases. Whatever might be the effect of extreme rates of passage, the curves give us a fairly reliable means of graphically correcting for the effect of speed within the limits which our experiments covered.

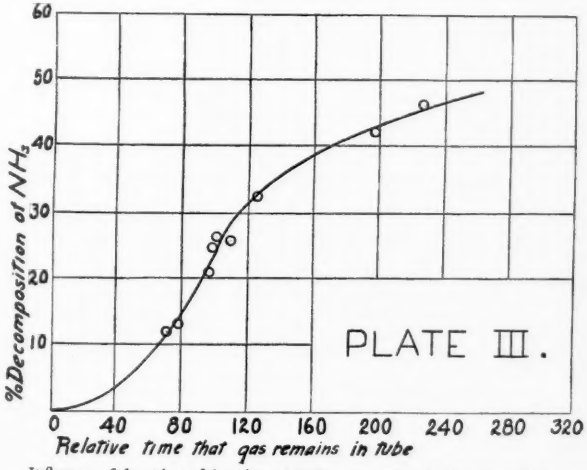
Tables IV to IX, inclusive, give the numerical data of the experiments on pure ammonia, ammonia with approximately its own volume hydrogen, ammonia with approximately its own volume nitrogen, ammonia saturated with water vapor at room temperature, ammonia with approximately its own volume carbon monoxide, and ammonia with varying amounts of carbon monoxide and saturated with water vapor. The last column in each table gives the percentage decomposition of the ammonia when correction has been made for speed according to the curves of Plate I, to a uniform speed of 125 cc. gases entering the tube per minute. The results thus obtained from Tables IV, V and VI for pure ammonia, ammonia and hydrogen, and ammonia and nitrogen are plotted in Plate II with temperatures as ordinates and per cent. decomposition of ammonia as abscissae. The point at which the rate of decomposition begins to be appreciable is placed at 450° from other experiments and corresponds with Ramsay and Young's statement of "a little below 500°." The twenty-three points arrange themselves on the curve as satisfactorily as could be expected. So far as we can tell from the curve the nitrogen and hydrogen have behaved absolutely as



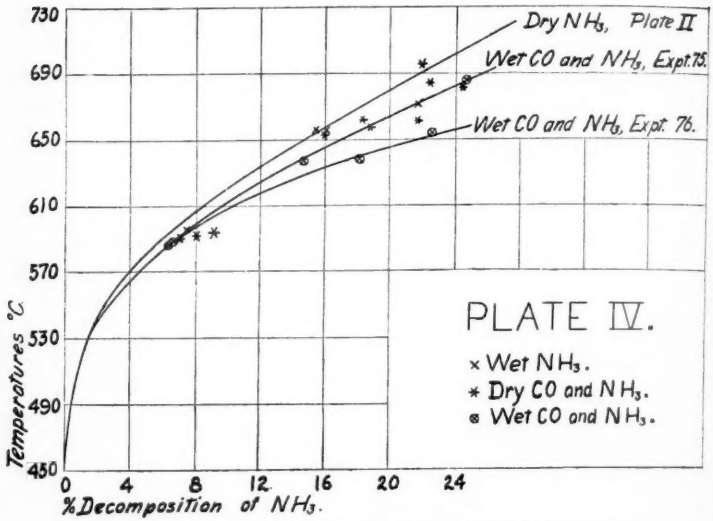
Relation between speed and ammonia decomposition. Curve A = 600° = 587-613°. B = 650° = 637°-663°. C = 690° = 677°-703°.



Relation between temperature and ammonia decomposition.



Influence of duration of heating at 690° upon ammonia decomposition.



Influence of carbon monoxide and water vapor upon ammonia decomposition.

indifferent gases. If there were any measurable tendency towards recombination of the nitrogen and hydrogen to form ammonia the equilibrium would be affected by the introduction into the ammonia of a large volume of one of the decomposition products. The proportion of ammonia decomposed does not appear to be affected by the introduction of an equal volume of hydrogen or nitrogen, therefore there is, apparently, no measurable tendency for nitrogen and hydrogen to recombine at these temperatures. If there is no equilibrium to limit the reaction, the decomposition of the ammonia should be complete at any temperature high enough to start decomposition, provided, only, that time enough be given.

The rate of decomposition is influenced to a very large extent by the physical state of the surface with which the gas is in contact. This was strikingly illustrated in one of our experiments. In the same apparatus, previously described, a new glass combustion tube was inserted, but this time the pyrometer tube was of glass instead of porcelain, all other conditions being the same. The decomposition was only about 2 per cent., as much as in the

former cases. The figures are given below, those for the porcelain pyrometer tube being taken from Plate II.

PERCENT DECOMPOSITION.

Temp. °C.	Porcelain pyrometer tube.	Glass pyrometer tube.
456°	0.0	0.0
568	4.0	0.10
627	10.8	0.15
688	21.5	0.46
723	28.6	0.61

Ramsay and Young, in the paper before referred to, have made somewhat similar observations. For instance, in their work they report that on passing ammonia through a glass combustion tube quite filled with fragments of broken glass tubing to increase the surface the decomposition amounted to 1.7 per cent., whereas on passing through a glass tube filled with ignited asbestos cardboard which, being porous, should expose a large surface to the gas, the decomposition was practically 100 per cent.

It is apparently not temperature then which is the important factor in causing decomposition, but the nature of the contact surface. It does not seem probable that substances as inert and nearly alike chemically as glass, porcelain and asbestos would exert any chemical influence. The difference would seem to be largely one of extent and physical nature of surface, and since surface is the all-important factor the inference follows that the decomposition must take place on the contact of the molecule with the surface.

This hypothesis is, in fact, entirely sufficient to explain all of our experimental results. The experiments of Ramsay and Young, and of Perman and Atkinson are also in harmony with the theory, so that, although it is not proven, it appears to the authors as the most satisfactory hypothesis to explain the decomposition of ammonia at high temperatures.

TABLE I.—INFLUENCE OF RATE OF FLOW ON DECOMPOSITION OF NH_3 AT 600°.

Expt. No.	Gas used.	Temp. °C.	Speed per minute.	Decomposition NH_3. Per cent.
73.1	CO and NH_3	595	92	11.2
67.1	NH_3	600	98	7.8
71.1	CO and NH_3	591	118	7.7
72.1	CO and NH_3	593	125	8.15
65.1	N and NH_3	597	124	6.8
66.1	N and NH_3	598	124	7.4
63.1	NH_3	599	125	6.5
74.4	NH_3 wet	596	138	6.9
64.1	NH_3	603	135	7.15
61.1	H and NH_3	613	146	6.5
62.1	H and NH_3	602	162	5.7

TABLE II.—INFLUENCE OF RATE OF FLOW ON DECOMPOSITION OF NH_3 AT 650°.

Expt. No.	Gas used.	Temp. °C.	Speed per minute.	Decomposition NH_3. Per cent.
72.4	CO and NH_3	652	82.0	25.7
72.2	CO and NH_3	661	90.4	27.0
74.5	NH_3 wet	655	119.0	17.4
66.2	N and NH_3	646	117.0	16.6
65.2	N and NH_3	652	119.0	17.3
73.2	CO and NH_3	660	129.0	21.0
71.2	CO and NH_3	657	132.0	17.5
64.2	NH_3	663	132.0	17.1
63.2	NH_3	662	135.0	14.4
62.2	H and NH_3	657	174.0	9.8

TABLE III.—INFLUENCE OF RATE OF FLOW ON DECOMPOSITION OF NH_3 AT 690°.

Expt. No.	Gas used.	Temp. °C.	Speed per minute.	Decomposition NH_3. Per cent.	Relative time heated.
64.4	NH_3	700°	55.0	46.2	227.0
73.3	CO and NH_3	695	63.0	42.2	196.0
72.3	CO and NH_3	680	99.0	32.5	125.0
71.3	CO and NH_3	684	113.0	25.9	110.0
64.3	NH_3	700	125.0	26.3	100.0
63.3	NH_3	700	128.0	24.6	98.0
67.3	NH_3	691	129.0	20.9	97.0
61.2	H and NH_3	677	161.0	13.1	77.0
62.3	H and NH_3	680	179.0	12.0	70.0

TABLE IV.—DECOMPOSITION OF PURE NH_3.

Expt. No.	Temp. °C.	Flow NH_3 per minute.	Decomposition. Per cent.	Decomposition corrected by Plate I to 125 cc. per minute. Per cent.
63.1	599	125	6.5	6.5
63.2	662	135	14.4	16.2
63.3	700	128	24.6	25.1
64.1	603	135	7.1	7.6
64.2	663	132	17.1	18.4
64.3	700	125	26.3	26.3
64.4	700	55	46.2	23.2
67.1	600	98	7.8	6.1
67.2	668	122	15.7	15.0
67.3	691	129	20.9	21.7

TABLE V.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES OF H AND NH_3.

Expt. No.	Temp. °C.	Flow H per minute.	Flow NH_3 per minute.	Total flow per minute.	Decomposition of NH_3. Per cent.	Decomposition NH_3 corrected to total flow of 125 cc. per minute. Per cent.
61.1	613	70.3	76.0	146.0	16.5	7.5
61.2	677	75.5	85.5	161.0	13.1	21.1
61.3	719	75.1	79.4	154.5	19.5	26.5
62.1	602	74.6	87.2	161.8	5.7	7.7
62.2	657	85.2	88.4	173.6	9.8	16.0
62.3	680	85.1	93.8	178.9	12.0	21.0
62.4	716	78.8	80.1	158.9	18.3	25.8
62.5	717	20.8	21.7	42.5	44.3	

TABLE VI.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES N AND NH_3.

Expt. No.	Temp. °C.	Flow N per minute.	Flow NH_3 per minute.	Total flow per minute.	Decomposition of NH_3 Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
65.1	597	62.2	61.7	123.9	6.8	6.8
65.2	652	63.9	55.1	119.0	17.3	16.1
65.3	667	61.2	56.4	117.6	20.6	18.3
66.1	598	62.8	61.1	123.9	7.4	7.4
66.2	646	61.1	55.8	116.9	16.6	14.3
66.3	672	58.9	54.3	113.2	23.5	20.0

TABLE VII.—DECOMPOSITION OF NH_3 SATURATED WITH WATER VAPOR AT ROOM TEMPERATURE.

Expt. No.	Temp. °C.	Flow NH_3 per minute.	Flow H_2O vapor per minute.	Total flow per minute.	Decomposition of NH_3 Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
74.2	655	104	3.0	107.0	19.2	15.5
74.3	670	132	4.0	136.0	19.7	21.7
74.4	596	133	5.0	138.0	6.9	7.5
74.5	655	114	5.0	119.0	17.4	16.2

TABLE VIII.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES OF DRY CO AND NH_3.

Expt. No.	Temp. °C.	Flow CO per minute.	Flow NH_3 per minute.	Total flow per minute.	Decomposition NH_3. Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
71.1	591	63.6	54.7	118.3	7.7	7.2
71.2	657	68.7	63.7	132.4	17.5	18.8
71.3	684	57.0	56.0	113.0	25.9	22.4
72.1	593	60.2	64.4	124.6	8.1	8.1
72.2	661	45.1	45.3	90.4	27.0	19.3
72.3	680	50.7	48.7	99.4	32.5	24.5
72.4	652	42.1	39.9	82.0	25.7	16.0
73.1	595	48.8	43.2	92.0	11.2	9.2
73.2	660	68.6	60.4	129.0	21.0	21.7
73.3	695	30.8	32.5	63.3	42.2	22.0

TABLE IX.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES CO AND NH_3 SATURATED COLD WITH WATER VAPOR.

Expt. No.	Temp. °C.	Flow H_2O per minute.	Flow CO per minute.	Flow NH_3 per minute.	Total flow per minute.	Decomposition NH_3. Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
75.1	587	4.2	9.2	93.2	106.6	7.9	6.4
75.2	637	4.3	12.7	88.9	105.9	18.7	14.7
75.3	685	4.0	22.6	90.4	117.0	27.2	24.7
76.1	589	5.1	46.0	54.4	105.5	7.9	6.8
76.2	638	4.8	47.1	65.5	117.4	19.6	18.2
76.3	653	4.3	41.6	63.8	109.7	25.9	22.7

The influence of duration of heating upon decomposition of ammonia is shown graphically for one temperature, 690°, in Plate III. The data for this curve are given in Table III.

There remains to be considered the influence of gases like carbon monoxide and water vapor which affect the decomposition

differently from the nitrogen and hydrogen before considered. Some experiments on the influence of these gases, which are not entirely inert, are given in Tables VII, VIII and IX, and in Plate IV. We note that the influence of a small amount of water vapor apparently increases the percentage decomposition of the ammonia, although there is only one set of tests on this point. Dry carbon monoxide increases the decomposition noticeably and rather irregularly. The decomposing influence of moist carbon monoxide is much more marked, increasing with the higher temperature and the proportion of carbon monoxide, as shown in Plate IV, where, for instance, in Expt. 76, a mixture of approximately three volumes of ammonia and two of carbon monoxide saturated with moisture at room temperature shows a decomposition of approximately 22 per cent. at 650° C., as compared with 14 per cent., shown by dry ammonia. In all the tests with carbon monoxide the cyanogen formation was measured by passing the escaping gases into dilute alkali and titrating the cyanide by silver nitrate. The yield of cyanogen was larger with the dry gases than the wet, but was in all cases small, the highest result obtained showing only about 4 per cent. of the ammonia decomposed converted into cyanide. No especial attention was paid to this question, and it is possible that by use of a suitable contact substance the yield could be largely increased.

The results of the foregoing paper may be summarized as follows: The temperature of initial ammonia decomposition is about 450° C. The percentage decomposition of ammonia gas when passing through a hot tube is not affected by dilution of the ammonia by an inert gas like hydrogen or nitrogen, provided the time which each ammonia molecule stays in the hot tube is not changed. In other words, if a liter of ammonia gas is to be passed through a hot tube at the rate of a liter a minute as much of it will be decomposed as if it were diluted with 9 liters of hydrogen or nitrogen, and the mixture passed through at the same rate of a liter a minute. This is confirmatory evidence of the views advanced by others that the decomposition of ammonia is irreversible and that there is no recombination of the nitrogen and hydrogen. The decomposition will, therefore, theoretically, become complete in a sufficient time. Gases, like carbon monoxide and water vapor, increase the rate of decomposition somewhat. The amount of cyanogen formed under the conditions of our

tests is very small. The influence of the nature of the hot surfaces, like porcelain or glass, is so great as to warrant the assumption that the decomposition takes place almost altogether on the impact of the ammonia molecule against the solid surface. With a rough surface a larger proportion of impinging molecules are decomposed than with a smooth surface. Experimentally, it has been found that ammonia gas in contact with a hot glass tube may be decomposed only slightly, while at the same temperature in contact with an equal extent of porcelain, the decomposition may be fifty times as great.

It follows as a conclusion that in the destructive distillation of coal, the decomposition of ammonia may be prevented by keeping the temperature low, and by lessening, so far as possible, the time which the red-hot gases remain in contact with rough substances like coke or the fire-clay retort. The introduction of blue water-gas into the retorts, as in the Lewes process, should, by rapidly sweeping out the gases, lessen the ammonia decomposition. The high yield of ammonia in the Mond gas producer may be assigned to the combination of lower temperature and rapid withdrawal of the gases.

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NOTE ON THE CONSTITUTION OF CERTAIN ORGANIC SALTS OF NICKEL AND COBALT AS THEY EXIST IN AQUEOUS SOLUTION.

BY O. F. TOWER.

Received January 28, 1905.

IN A former paper[1] it was shown that the nickel and cobalt salts of succinic, malic and tartaric acids exist in a polymerized state in aqueous solution, and that this polymerized condition becomes more noticeable the more hydroxyl groups are present in the molecule; that is, the tartrates are more polymerized than the malates, and these latter than the succinates. These facts were brought out by means of measurements of the electrical conductivity and determinations of the depression of the freezing-point of solutions of these salts. An extension of these determinations[2] to the salts of malonic and tartronic acids showed

[1] This Journal, **24**, 1012 (1902).
[2] *Loc. cit.*, pp. 1020–1022.

that the salts of the latter were no more polymerized than those of the former, that is, that the hydroxyl group in this case apparently did not increase polymerization of the molecules. It was, however, stated at the time that this was probably an exceptional case, as the lowest members of many of the organic series exhibit peculiar behavior.

To throw further light on this subject, I have recently extended these investigations to the salts of the glutaric acid series. The nickel, cobalt, and magnesium salts of glutaric, α-hydroxyglutaric, and trihydroxyglutaric acids have been prepared and their conductivity and freezing-points determined. The first of these acids was a preparation of Merck, the second of Gerhardt, and the last was made by myself from arabinose, according to the method of Kiliani.[1] The yield of trihydroxyglutaric acid was small, but after crystallizing from alcohol enough was obtained to prepare the three salts in sufficient quantity to make one complete series of determinations. The solutions were prepared in the manner detailed in the paper already referred to, and almost all of the phenomena mentioned there were observed here. All of the solutions, except that of magnesium trihydroxyglutarate, which seemed to be exceptionally soluble, were practically saturated. The analyses of the solutions and the details of the measurements were likewise the same as before. The conductivity of the water used in preparing the solutions was 1.8×10^{-6}. This was subtracted from the conductivity of the solutions. The molecular conductivity, M, of the salts is shown in Table I; v represents the number of liters in which a gram-molecule of the salt was dissolved.

TABLE I.

NICKEL GLUTARATE.

v	M	v	M
33.15	84.7	34.47	91.3
2×33.15	99.3	2×34.47	106.4
4×33.15	115.9	4×34.47	122.3
8×33.15	129.9	8×34.47	135.4
16×33.15	142.7	16×34.47	147.1
32×33.15	154.5	32×34.47	157.7
64×33.15	165.6	64×34.47	167.8

[1] *Ber. d. chem. Ges.*, **21**, 3007 (1888).

MAGNESIUM GLUTARATE.

v	M	v	M
22.80	87.5	25.56	86.8
2×22.80	96.7	2×25.56	97.6
4×22.80	107.7	4×25.56	108.6
8×22.80	119.4	8×25.56	119.5
16×22.80	130.4	16×25.56	131.1
32×22.80	140.7	32×25.56	141.8
64×22.80	149.2	64×25.56	152.4

COBALT HYDROXYGLUTARATE.

v	M	v	M
23.48	67.1	24.16	66.6
2×23.48	81.6	2×24.16	81.0
4×23.48	97.6	4×24.16	95.3
8×23.48	110.0	8×24.16	109.9
16×23.48	125.3	16×24.16	123.1
32×23.48	138.8	32×24.16	137.5
64×23.48	150.6	64×24.16	151.1

COBALT GLUTARATE.

v	M	v	M
31.38	90.7	29.70	86.7
2×31.38	104.5	2×29.70	101.3
4×31.38	118.6	4×29.70	114.7
8×31.38	132.8	8×29.70	129.3
16×31.38	146.7	16×29.70	143.7
32×31.38	158.5	32×29.70	155.4
64×31.38	170.0	64×29.70	165.3

NICKEL HYDROXYGLUTARATE.

v	M	v	M
33.31	71.3	30.41	71.4
2×33.31	87.3	2×30.41	86.6
4×33.31	102.8	4×30.41	101.9
8×33.31	121.8	8×30.41	116.6
16×33.31	138.8	16×30.41	132.2
32×33.31	156.2	32×30.41	147.0
64×33.31	168.9	64×30.41	161.2

MAGNESIUM HYDROXYGLUTARATE.

v	M	v	M
21.54	85.1	23.32	88.4
2×21.54	98.6	2×23.32	101.9
4×21.54	113.2	4×23.32	115.5
8×21.54	127.7	8×23.32	127.6
16×21.54	139.5	16×23.32	139.4
32×21.54	151.3	32×23.32	150.7
64×21.54	161.0	64×23.32	160.6

Nickel Trihydroxyglutarate.		Cobalt Trihydroxyglutarate.		Magnesium Trihydroxyglutarate.	
v	M	v	M	v	M
39.13	53.0	42.14	51.6	10.600	38.8
2×39.13	62.8	2×42.14	62.9	2×10.600	47.8
4×39.13	72.4	4×42.14	74.7	4×10.600	57.8
8×39.13	82.6	8×42.14	89.1	8×10.600	70.3
16×39.13	92.1	16×42.14	100.6	16×10.600	84.0
32×39.13	101.6	32×42.14	116.0	32×10.600	99.0
64×39.13	111.6	64×42.14	131.6	64×10.600	114.9
				128×10.600	130.7

From these results, interpolations have been made graphically for the dilutions, $v=16$, 32, etc. These interpolated values are given in Table II. In cases where the conductivity was determined in duplicate, only the averages are given in the table.

Table II.

Molecular Conductivity of Glutarates.

v.	Nickel.	Cobalt.	Magnesium.
16	..	..	81.8
32	87.0	89.5	91.0
64	102.1	103.4	101.4
128	117.8	117.6	112.7
256	131.5	131.9	124.1
512	143.9	145.9	135.3
1024	155.3	157.6	145.1
2048	165.9	168.3	154.5

Molecular Conductivity of Hydroxyglutarates.

v.	Nickel.	Cobalt.	Magnesium.
16	....	....	80.0
32	71.6	72.9	93.7
64	87.1	87.5	107.7
128	102.4	101.7	121.1
256	119.0	116.3	134.0
512	134.6	130.5	145.6
1024	151.7	143.7	156.3
2048	165.4	155.6	165.7

Molecular Conductivity of Trihydroxyglutarates.

v.	Nickel.	Cobalt.	Magnesium.
16	....	....	43.6
32	50.1	47.0	52.0
64	60.0	58.5	64.0
128	69.5	69.8	78.2
256	79.3	83.0	92.9

v.	Nickel.	Cobalt.	Magnesium.
512	89.2	96.8	108.0
1024	99.1	110.5	124.0
2048	108.8	125.5	140.2

Although the conductivity of the cobalt and nickel salts is, in general, somewhat greater than the conductivity of the corresponding salts of malic and tartaric acids, still the conductivity seems to decrease as the number of hydroxyl groups increases in a manner quite similar to that of the succinic acid series.

The depression of the freezing-point for different solutions of these salts is given in Table III, together with the apparent molecular weights calculated from them.

TABLE III.

NICKEL GLUTARATE. Mol. wt. = 189.

Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
0.5508	0.121°	84
0.5476	0.108	94
0.2754	0.065	78
0.2738	0.059	86
0.1377	0.033	77
0.1369	0.031	82

COBALT GLUTARATE. Mol. wt. = 189.

Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
0.6365	0.119°	99
0.6144	0.118	96
0.3183	0.063	94
0.3072	0.061	93
0.1592	0.038	78
0.1536	0.032	89

MAGNESIUM GLUTARATE. Mol. wt. = 154.

0.6769	0.127°	99
0.6038	0.114	98
0.5077	0.100	94
0.3019	0.064	87
0.2538	0.055	85
0.1510	0.033	85

NICKEL HYDROXYGLUTARATE. Mol. wt. = 205.

0.6733	0.108°	115
0.6147	0.106	107
0.3367	0.058	107
0.3024	0.054	105
0.1864	0.030	104
0.1512	0.029	98

COBALT HYDROXYGLUTARATE. Mol. wt. = 205.

0.8734	0.148°	109
0.8487	0.147	108
0.4367	0.077	103
0.4244	0.075	105
0.2184	0.043	94
0.2122	0.041	96

MAGNESIUM HYDROXYGLUTARATE. Mol. wt. = 170.

0.7907	0.164°	89
0.7304	0.141	96
0.3954	0.083	88
0.3652	0.074	91
0.1977	0.044	83
0.1826	0.042	80

Nickel Trihydroxyglutarate. Mol. wt. = 237.			Cobalt Hydroxyglutarate. Mol. wt. = 237.		
0.6050	0.080°	140	0.5625	0.072°	145
0.3025	0.042	317	0.2813	0.037	141
0.1513	0.025	112	0.1407	0.021	124

Magnesium Trihydroxyglutarate.

Mol. wt. = 202.

1.9087	0.293°	121
0.9544	0.154	115
0.4772	0.092	96

When we compare the apparent molecular weight with the molecular weight calculated on the basis of the simple formula in the above table there appears to be but little evidence of polymerization. In the case of the tartrates of nickel and cobalt, apparent molecular weights were obtained which exceeded the calculated molecular weights, and this was the reason for postulating polymerization in those cases. Since, however, the trihydroxyglutarates yield somewhat higher apparent molecular weights than the other glutarates and also molecular conductivities, it can be said that, if there is any tendency toward polymerization of these salts, it is strongest when the maximum number of hydroxyl groups are present in the molecule.

It may, however, be stated that the tendency toward polymerization shown by the cobalt and nickel salts of malates and tartrates apparently grows no stronger with similar salts of the higher hydroxy-acids of this series.

Western Reserve University,
January, 1905.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

RADIOACTIVITY AS AN ATOMIC PROPERTY.

By Herbert N. McCoy.

Received February 18, 1905.

It is now generally considered that the radioactivity of any element is independent of its form of chemical combination, that, in fact, radioactivity is a property of the atom rather than of the molecule. There is already much evidence in favor of this view. Thus it is well established that the rate of decay of activity of temporarily radioactive products is wholly independent of all

chemical as well as physical conditions.[1] Further, all compounds of radium and uranium are active, as are also, probably, all those of thorium.[2] The radioactivity of pure uranium compounds is roughly proportional to the percentage of uranium.[3]

Table I shows the results obtained by Mme. Curie for the activities of a number of uranium compounds, in terms of the saturation current, i, in amperes. It is apparent that the greatest activity is shown by those compounds richest in uranium. I have calculated the ratio of the current to the percentage, P, of uranium. The ratio is of the same order for all compounds, but it is by no means constant.

TABLE I.

	P.	$10^{11}i$.	$\frac{10^{13}i}{P}$.
Metallic uranium	100	2.3	2.3
Uranium oxide black	86	2.6	3.0
" " green	85	1.8	2.1
Uranic acid	72	0.6	0.8
Sodium uranate	75	1.2	1.6
Potassium "	72	1.2	1.7
Ammonium uranate	76	1.3	1.7
Urano sulphate	48	0.7	1.5
Uranyl "	56	1.2	2.1
" nitrate	47	0.7	1.5

In connection with a study of the relative activities of uranium ores and pure compounds of uranium,[4] I have also made some measurements of a similar nature, the results of which are reproduced in Table II. Here θ is the time of discharge of the electroscope through a certain number of divisions of the scale of the micrometer microscope. The radioactivity is inversely proportional to θ. P is the percentage of uranium and $K = \frac{10^5}{P \times \theta}$.

TABLE II.

	Formula.	θ.	P.	K.
1	U_3O_8	259	85	4.55
2	U_3O_8[5]	270	85	4.37
3	$UO_2(OH)_2$	303	72	4.59
4	$UO_2(NO_3)_2.6H_2O$	650	47	3.27
5	$UO_2(C_2H_3O_2)_2.2H_2O$	492	56	3.62
6	$UO_2(C_2H_3O_2)_2.2H_2O$	545	56	3.28
				Mean, 3.86

[1] P. Curie: *Soc. Phys.*, 1900, p. 20; *Compt. Rend.*, **136**, 225 (1903). Becquerel: *Ibid.*, **133**, 199 (1901); Rutherford and Soddy: *Phil. Mag.* [6], **4**, 385 (1902).

[2] Inactive thorium has been reported by Hofmann and Zerban, *Ber. d. chem. Ges.*, **36**, 3093 (1903) and by Baskerville and Zerban, This Journal, **26**, 1642 (1904).

[3] Mme. Curie: *Thèse*, Paris (1903); also *Chem. News*, **88**, 98 (1903); McCoy: *Ber. d. chem. Ges.*, **37**, 2641 (1904).

[4] McCoy: *Loc. cit.*; Boltwood: *Am. J. Sci.*, **18**, 97 (1904).

[5] Two different samples of each the oxide and acetate were studied.

It was found that the ratio of the activity to the percentage of uranium was more nearly constant for the ores than for the pure compounds. But the activity constant, K, was approximately 5.7 times as great for the ores as for the pure substances. This excess of activity of the ores is due to radium. It would follow that imperfect purification in the process of preparation might give products containing more or less radium, and therefore abnormally active. The question whether the radioactivity of all pure uranium compounds is directly proportional to the percentage of uranium and whether radioactivity is really an atomic property was so important that further study was devoted to the problem, with the results here reported.

The following experiment showed conclusively that the above-mentioned suggestion is inadequate to explain the variability of K, for which a constant value might be expected. Five grams of pure uranyl nitrate $UO_2(NO_3)_2.6H_2O$ (C. A. F. Kahlbaum's best grade) gave upon ignition 2.802 grams of U_3O_8; calculated, 2.797 grams. The ratio of the activities of 0.5-gram portions of the oxide, so obtained, and of the original nitrate were as 356 to 115. The measurements were made with an electroscope in the manner previously described.[1] The percentages of uranium are 85 and 47 respectively, from which K equals 4.2 and 2.5. In this experiment the two compounds must have contained the same proportion of radioactive impurity (radium), if any at all were present. The non-agreement of the two values of K is due to an entirely different cause.

Mme. Curie had shown[2] that the effective activity, as measured by the conductivity method, of any uranium compound, spread uniformly upon a given area, is nearly independent of the thickness of the layer, for layers between 0.5 and 3 mm. thick. This result was confirmed by Rutherford and McClung[3] who found that in the case of uranium oxide the maximum activity was practically reached for a weight of 0.035 gram per square centimeter. Taking the density of U_3O_8 as 7.2, such a layer would be about 0.05 mm. thick. This effect is due to the great absorption of the α-rays, which are the chief cause of ionization, by the uranium compound itself. The absorption of the Becquerel and cathode rays by screens of inert matter has been extensively

[1] McCoy: *Loc. cit.*
[2] *Loc. cit.*
[3] *Phil. Trans. A*, 1901, p. 25.

studied. The intensity, I, of the rays after passing through a thickness, x, of the screen is expressed by $I = I_0 e^{-\lambda x}$, where I_0 is the initial intensity and λ the absorption constant for unit thickness. It has been shown by Strutt[1] that the coefficient of absorption of the β-rays of radium by various forms of matter is nearly proportional to the density of the absorbing screen. Leonard[2] had found a similar result for cathode rays.

It has been shown[3] that the α-rays of all compounds of the same radioactive element have the same power of penetration for screens of inert material. Experiments of Rutherford and Miss Brooks[4] show that the coefficients of absorption of the α-rays of thorium, radium and uranium by aluminium and by air are approximately proportional to the densities of these two substances. Considering these facts, it seemed possible that the coefficients of absorption of the α-rays by the uranium compounds themselves might be proportional to their densities; and therefore that for equal weights of all uranium compounds spread uniformly upon equal areas the observed activities, as measured electrically, should be proportional to the percentages of uranium. The results shown in Tables I and II indicated that either such a simple absorption law did not apply in the case of the radiations of uranium, or that radioactivity is not strictly an atomic property. As will be shown subsequently, the former of these alternative suggestions is the true explanation of the facts.

If a thin layer, of weight w, of a radioactive substance is spread uniformly upon a metal plate of area s, and if A is the observed activity, as measured electrically, it is readily shown that

$$\frac{d\,A}{d\,w} = \tfrac{1}{2}\left(k_1 - \frac{k_2 A}{s}\right) \qquad (1)$$

where k_1 is the total activity of unit mass for no absorption of the rays, and k_2 is the constant of absorption for unit mass of substance upon unit area.[5] The factor $\frac{1}{2}$ is used, since half of the rays are directed downward, and are absorbed by the metal plate. Integration of (1) gives[6]

[1] *Nature*, **61**, 539 (1900).

[2] *Wied. Ann.*, **56**, 255 (1895).

[3] Mme. Curie: *Loc. cit.*; Rutherford: *Phil. Mag.*, [5], **47**, 117 (1899); Owens: *Ibid.*, **48**, 360 (1899).

[4] *Phil. Mag.* [6], **4**, 6 (1902).

[5] If λ is the coefficient of absorption for unit thickness; $k_2 = \dfrac{\lambda}{\text{density}}$.

[6] Cf. Rutherford and Grier: *Phil. Mag.* [6], **4**, 327 (1902).

$$A = \frac{k_1 s}{2k_2}\left(1 - e^{-\frac{k_2 w}{s}}\right). \quad (2)$$

For all but small values of w, $e^{-\frac{k_2 w}{s}}$ is practically zero, and

$$A = \frac{k_1 s}{2k_2} = A_1 \quad (3)$$

where A_1 is the maximum value of the function. Therefore

$$A = A_1(1 - e^{-\frac{k_2 w}{s}}). \quad (4)$$

By means of the last equation it is possible to determine k_2 and k_1 from the observed activities of layers of different weights.

$$\text{If } \frac{A}{A_1} = x,$$

then

$$k_2 = \frac{2.303\, s}{w} \log \frac{1}{1-x}. \quad (5)$$

I have found that when finely powdered uranium oxide is sifted on a plate, so as to obtain a fairly uniform distribution, the maximum activity is practically reached for about 0.02 gram per sq. cm. The thickness of such a layer is about 0.03 mm. This result agrees well with that obtained by Rutherford and McClung[1] by the same method. It was found to be almost impossible by the method of sifting to get perfectly uniform layers much thinner than 0.03 mm. This is not remarkable, since the finest bolting-cloth obtainable had meshes of 0.1 mm. The desired result was accomplished by grinding the uranium compound in an agate mortar with a volatile liquid in which the compound was insoluble and then pouring the liquid, containing the suspended substance, into a shallow flat-bottomed metal dish. This was covered with a cover-glass until the sediment had settled. When the liquid had evaporated the solid was left in the form of a thin, exceedingly uniform film. In some cases this was not more than 0.0005 mm. in thickness. Chloroform and ethyl and methyl alcohols were used as the suspending liquids.

The measurements of radioactivity were made with an electroscope as previously described.[2] The sensitiveness of the electroscope varied somewhat from day to day. The maximum change was about 3 per cent., as shown by measurements of the activity of a certain portion of uranium oxide used as a standard. Usually five determinations of the activity of each film were

[1] *Loc. cit.*

[2] McCoy: *Ber. d. chem. Ges.*, **37**, 2648 (1904).

made, and the average taken. For the same film successive averages so found did not differ by as much as ½ per cent. In order to detect any possible change in the sensibility of the electroscope, determinations with the standard sample were made immediately before and after every set of measurements made with each film. The ratio of the activity of the standard to that of any film remained quite constant from day to day as the following results obtained on different days show: 2.152, 2.158, 2.157, 2.164; also in another case: 0.9916, 0.9917, 0.9934, 0.9933, 0.9966, 0.9917. The variations in the sensitiveness of the instrument did not, therefore, cause appreciable errors in the determinations of relative activity.

Thus far, three pure compounds of uranium have been systematically examined. These are the oxide, U_3O_8; the oxalate, $UO_2C_2O_4.3H_2O$; and ammonium uranate, $(NH_4)_2U_2O_7$. Good films of the nitrate could not be obtained because no volatile liquid could be found in which the finely powdered nitrate would remain suspended. The oxalate is obtained as a yellow crystalline meal upon mixing solutions of the nitrate and oxalic acid.[1] Kahlbaum's purest uranium nitrate was used as the starting material in all cases. Analysis of the hydrated salt: 1.6108 grams at 105° lost 0.1432 gram of H_2O; 0.5783 gram gave upon ignition 0.3925 gram of U_3O_8.

	Calculated for $UO_2C_2O_4.3H_2O$.	Found.
$3H_2O$	8.70	8.89
U	57.82	57.59

The dried salt, from the above determination of water of crystallization, took up moisture rapidly when exposed at ordinary temperature to the air of the laboratory.[2] The gain in forty minutes was one-fourth of the total water lost. After twenty-four hours the gain was 0.1414 gram. This represents 8.69 per cent of the weight of the hydrated salt. The oxalate is not very soluble in water, and is not deliquescent. Since it was possible that a trace of radium might be present in the original nitrate, the activity of a quantity of oxide obtained by direct ignition of the nitrate was compared with that of the oxide resulting from the oxalate. There was no detectable difference in activity. In transformations of uranium compounds radioactive impurities usually concentrate in either the precipi-

[1] Peligot: *Ann. Chem.* (Liebig), **43**, 282 (1842); Ebelmen: *Ibid.*, **43**, 287 (1842).

[2] This was in December, when the outside air was very dry.

tate or in the mother-liquor. It, therefore, seemed probable that no appreciable amount of such impurities was present. Table III gives the results obtained with uranium oxalate. Ethyl or methyl alcohol was used as the suspending liquid.

TABLE III.

	w.	x.	$\frac{w}{x}$.	k_2.
1	0.0558	0.505	0.1105	507
2	0.0654	0.558	0.1172	501
3	0.0763	0.616	0.1239	504
4	0.0766	0.621	0.1233	509
5	0.0870	0.669	0.1301	510
6	0.1035	0.730	0.1418	508
7	0.1095	0.752	0.1456	511
8	0.2771	0.99	0.280	.....
9	0.4235	1.00	0.424	.....
10	0.6491	1.00	0.649	.....
			Mean,	507

The circular metal dishes used all measured 7.15 cm. in diameter. Therefore, the area, s, was 40.15 sq. cm. for each film; w is the weight of substance spread upon the area s; x is the ratio of the activity of any film to that of No. 10, which had the maximum activity. The results given in Table III are shown graphically in Fig. 1. For Curve I the ordinates are proportional to $x = \frac{A}{A_1}$; for Curve II to $\frac{w}{x}$; the abscissas are proportional to w in both cases.

Uranouranic oxide, U_3O_8, was obtained by igniting the oxalate.[1] The best films were obtained by the use of chloroform. Table IV gives the results for the oxide.

TABLE IV.

	w.	x.	$\frac{w}{x}$.	k_2.
1	0.0084	0.0663	0.127	328
2	0.0206	0.1521	0.136	321
3	0.0339	0.2495	0.136	340
4	0.0433	0.3001	0.144	331
5	0.0471	0.3220	0.146	331
6	0.0526	0.3535	0.149	333
7	0.0609	0.3817	0.160	317
8	0.0716	0.4520	0.159	337
9	0.1725	0.7755	0.222	348
10	0.2342	0.8774	0.267	360
11	0.3281	0.98	0.335	.....
12	0.5617	1.00	0.562	.....
			Mean,	335

[1] Zimmermann: *Ann. Chem.* (Liebig), **232**, 276 (1885).

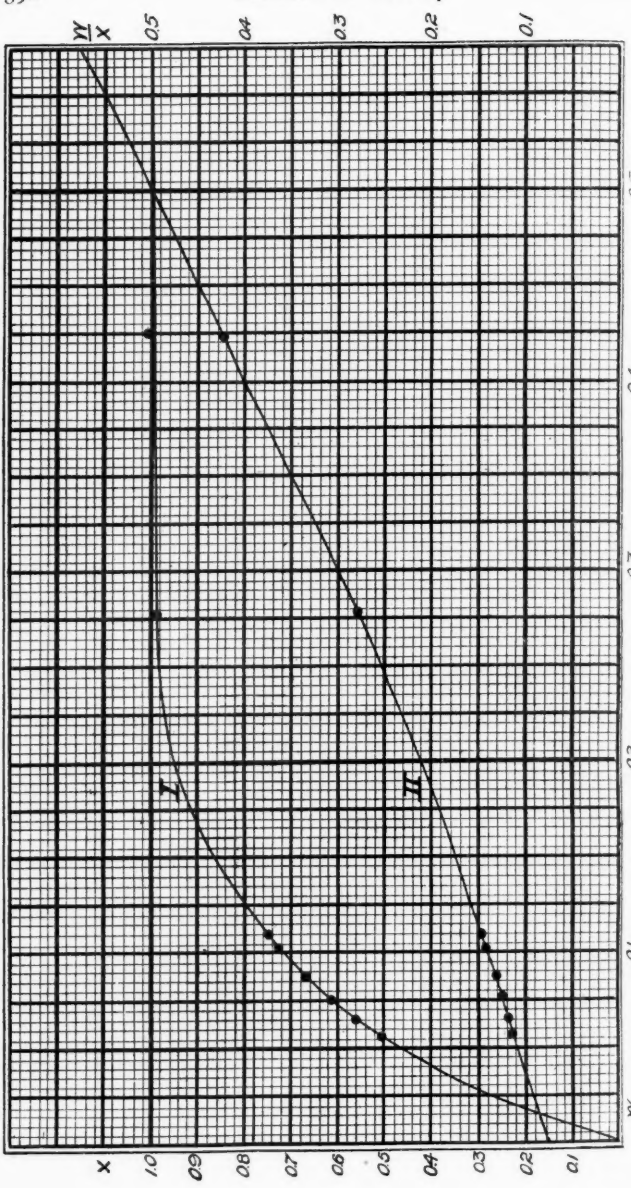


Fig. 1. Uranium oxalate.

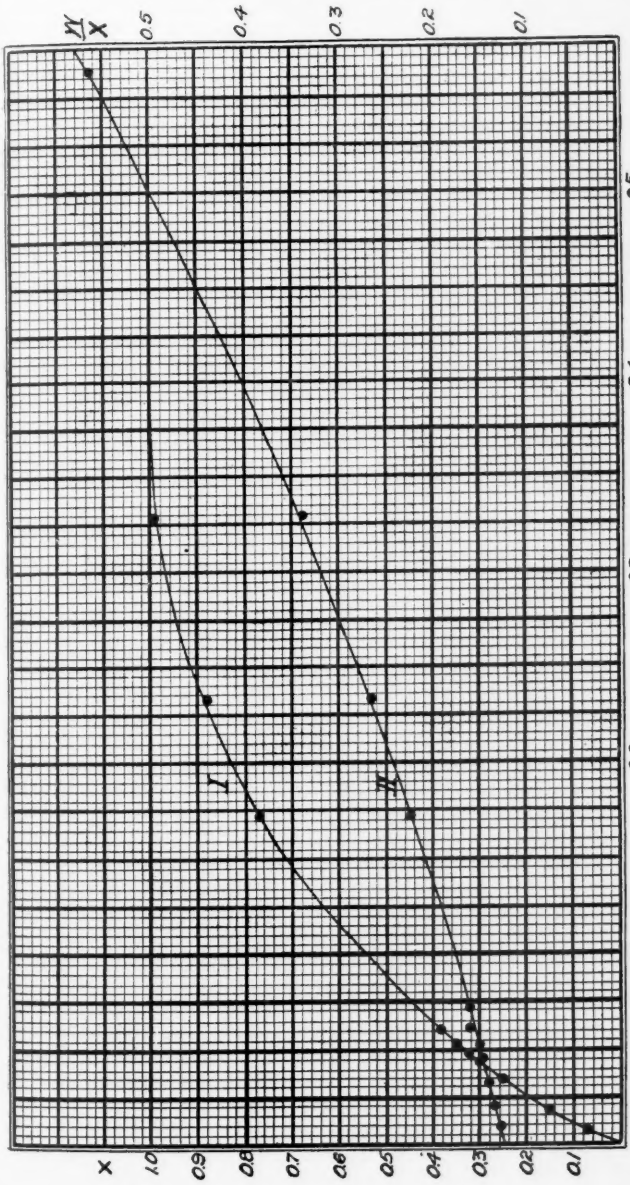


Fig. 2. Uranium oxide.

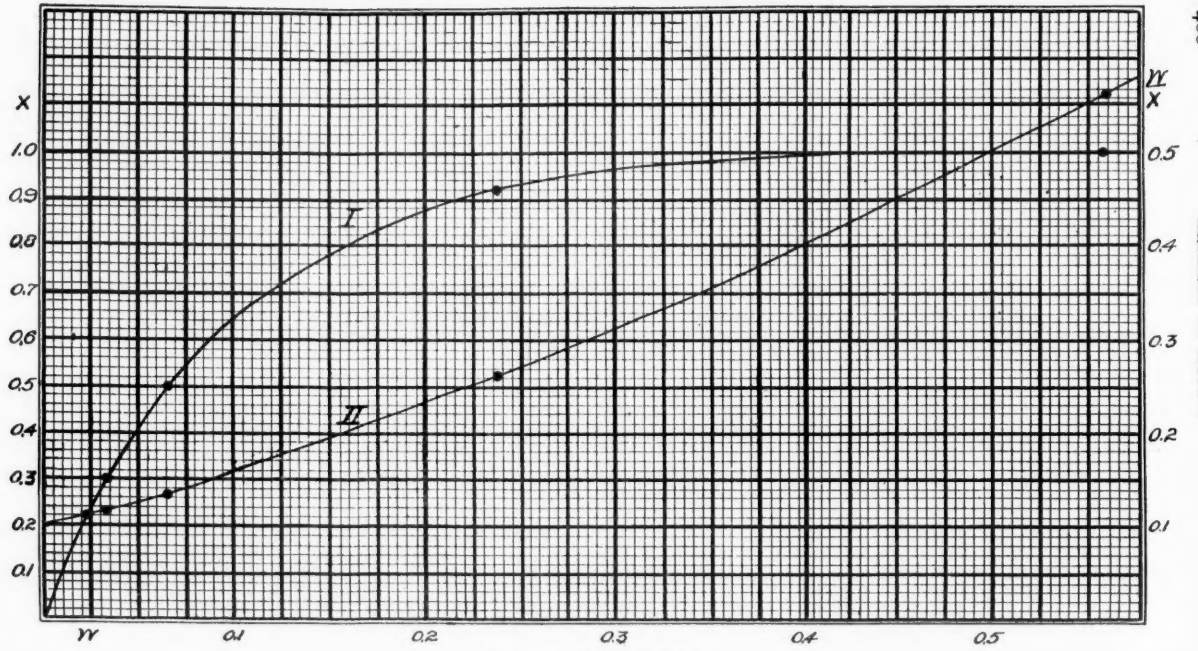


Fig. 3. Ammonium uranate.

The curves for the oxide are given in Fig. 2.

Similar, but less complete measurements were made with ammonium uranate. This substance was obtained by precipitating uranium nitrate with ammonium hydroxide. The precipitate was carefully washed and dried, finally at 140°. Analysis: 0.2274 gram of the substance gave upon ignition 0.1992 gram U_3O_8, equal to 74.4 per cent. uranium, calculated for $(NH_4)_2U_2O_7$, 76.4 per cent. It is probable that the substance prepared as above does not have a perfectly definite composition. Table V gives the results obtained with ammonium uranate, the films of which were deposited from alcohol.

TABLE V.

	w.	x.	$\frac{w}{x}$.	k_2.
1	0.0238	0.2185	0.109	420
2	0.0338	0.2983	0.114	415
3	0.066[1]	0.5[1]	0.132	416
4	0.2367	0.914	0.259	416
5	0.5620	1.00	0.562	.....
			Mean,	417

Fig. 3 shows the curves for ammonium uranate.

The values of k_2 are nearly constant for a given substance, but differ greatly for different substances. These results may now be used to calculate the *total* activities of unit weights of each of the uranium compounds. From (3)

$$k_1 = \frac{2k_2A_1}{s}. \qquad (6)$$

The relative values of A_1 for the three compounds are given in the first column of Table VI. These figures represent the relative values of the reciprocals of the times of discharge of the electroscope for layers of maximum activity. The area, s, was the same in all cases and equal to 40.15 sq. cm. The values of k_1 are calculated on the basis of A_1, equal to unity for the oxide. P is the proportion of uranium in each substance.

TABLE VI.

	A_1.	k_2.	k_1.	P.	$\frac{k_1}{P}$.
Oxide	1.000	335	16.69	0.849	19.7
Oxalate	0.459	507	11.59	0.576	20.1
Uranate	0.720	417	14.95	0.744	20.1
				Mean,	20.0

[1] By graphic interpolation.

Fig. 3. Ammonium uranate.

If radioactivity is an atomic property $\frac{k_1}{P}$ should be a constant. The results seem to justify this conclusion.

There is still another way to determine the value of k_1. The curves for $\frac{w}{x}$ may be continued until they cut the axis of ordinates. The point of intersection of any curve represents the theoretical value of w for an infinitely thin film. Since for such a film there would be no absorption $A = \frac{1}{2}k_1 w$ and $k_1 = \frac{2A}{w} = \frac{2A_1 x}{w}$. The values of w as found by such graphical extrapolation are given in column one, Table VII. The fourth column gives for comparison the values of (k_1) as found by the first method.

TABLE VII.

	$\frac{w}{x}$.	A_1.	k_1.	(k_1).	P.	$\frac{k_1}{P}$.
Oxide.....	0.123	1.000	16.26	16.69	0.849	19.2
Oxalate	0.0825	0.459	11.13	11.59	0.576	19.3
Uranate	0.0995	0.720	14.47	14.95	0.744	19.5
					Mean,	19.3

The average value of $\frac{k_1}{P}$ is 19.7. This represents the total activity of the α-rays of unit weight of metallic uranium when the maximum activity of a layer of uranium oxide 40.15 sq. cm. in area is taken as unity. Instead of employing arbitrary units, $k_1 P$ may be expressed in terms of the saturation current which would be due to the ionization caused by the α-rays of one gram of the element uranium, providing there was no absorption of the rays. Rutherford and McClung[1] have found the maximum saturation current due to the α-rays of a layer of uranium oxide to be about 4.5×10^{-13} amperes per square centimeter. Therefore, $A_1 = s \times 4.5 \times 10^{-13}$ amperes, and $\frac{k_1}{P} = 19.7 A_1 = 3.6 \times 10^{-10}$ amp.

Summary.—1. These experiments show that the effective (or directly observed) activity of the layers of uranium compounds sufficiently thick to show the maximum α-ray activity depends not only on the uranium content but also on the coefficient of absorption of the rays by the radioactive substance itself. 2. A method of determining such absorption coefficients has been worked out. 3. It is further shown that, when absorption is taken

[1] *Loc. cit.*

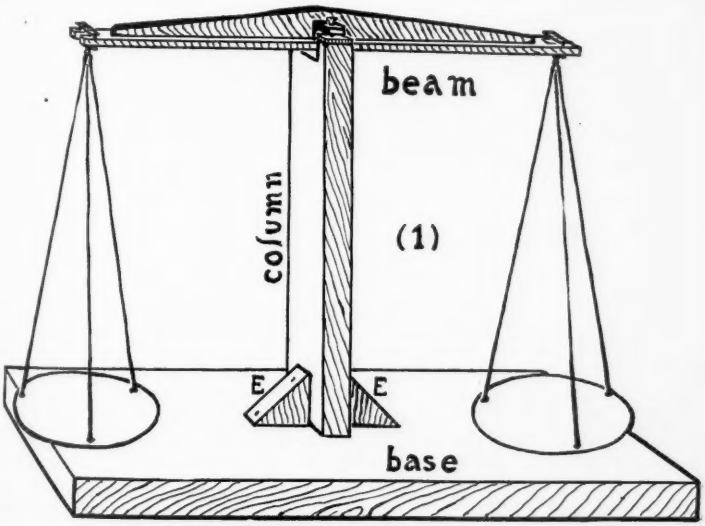
into account, the *total* α-ray activity of any uranium compound is strictly proportional to its percentage of uranium. This is a direct confirmation of the theory that radioactivity is an atomic property.

February 8, 1905.

NOTE.

A Home-made balance.—It is thought that the balance figured below may prove useful in schools to illustrate the law of conservation of mass, and for other chemical and physical experiments. It can be made for less than a dollar; and when carrying a kilogram on each arm, half a gram additional is enough to move the pans through three inches.

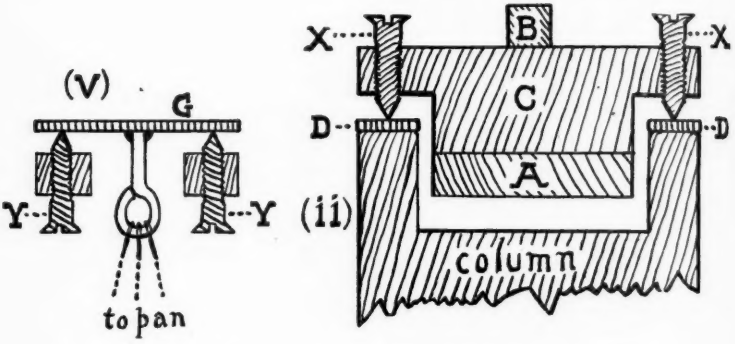
In the figure (i) shows the balance in perspective, (ii) is a trans-



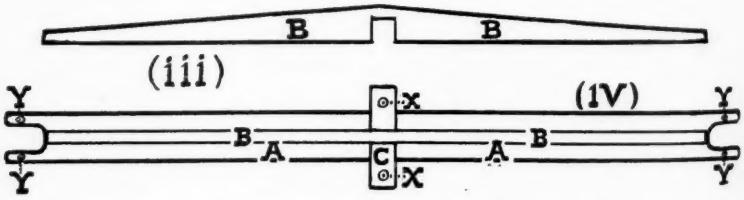
verse section through the beam, column and screws which serve as "knife edges," (iii) is the stiffening piece, (iv) is a view of the beam from above, and (v) is a section through the beam near the end, to show how the pans are supported.

The base is a piece of board 8 x 30 inches. *The column* is of

wood, 3 inches from front to back of (i), 1 inch from right to left, and 18 inches high, screwed to the base and supported by two triangular pieces E; a notch $\frac{5}{8}$ inch deep x $1\frac{3}{4}$ inches is cut out of the top, as shown (in ii), and two small pieces of brass are screwed on at D. *The beam* is a lath, A, 25 inches long, $\frac{1}{4}$ inch thick and



$1\frac{1}{2}$ inches wide, with a notch at each end $\frac{5}{8}$ inch wide and 1 inch long; it is stiffened by a vertical piece, B, of the same thickness, 23 inches long and 1 inch high in the center, tapering to both ends and fastened to A by screws. A transverse piece, C, of the shape shown in (ii) and (iv) carries two screws, X (flat head bright, 1 inch No. 6), whose points are filed sharp and rock on the plates, D. Four more screws Y ($\frac{3}{4}$ inch No. 4), two at each end of the beam, carry small pieces of brass, G ($1\frac{1}{2}$ x $\frac{3}{8}$ inches), to each of which is soldered a wire loop; *the pans*, of galvanized iron, $6\frac{1}{2}$ inches diameter, are hung from the loops by three strings



each, so as to come about 3 inches above the base. Punch marks may be made in the brass plates, G, to keep them from slipping off the screw points; the plates, D, should be left smooth.

The points of the six screws, X, Y, and the center of gravity of the beam should be nearly in the same plane; the delicacy of the balance is increased by screwing down the two screws, X; if they are too low, however, the beam will overbalance on either side and will not rise. The balance should be adjusted once for all, best when weighted; a pointer with small adjustable weight may be added, if desired. W. LASH MILLER.

REVIEW.

SOME ABSTRACTS FROM RECENT FOREIGN LITERATURE UPON INDUSTRIAL CHEMISTRY.

BY FRANK H. THORP.

Received February 2, 1905.

IN THE preparation of this article the purpose has been to bring together some of the papers published in the foreign journals during the past year, and which have not been included in the *Review of American Chemical Research*. In the interests of brevity exhaustive reviews have not been attempted and only the more prominent points have been touched upon. Several articles are the continuation of work abstracted in this Journal, **26**, 192.

TECHNICAL EDUCATION.—The teaching of Industrial Chemistry and Chemical Engineering continues to receive much attention in papers and addresses before scientific societies. Frequent references to it were made by Sir William Ramsay during his tour of this country last summer, and by other authors in papers read at the St. Louis Congress for Applied Chemistry. The subject was also referred to; and an extended review of the situation in America appears in the reports of the Mosely Educational Commission, issued early in 1904. Procter (*J. Soc. Chem. Ind.*, 1904, 1074) discusses the relation of the University to Technology in his annual address to the Yorkshire section of the Society of Chemical Industry. Dealing with the question mostly from the British standpoint, he finds conditions in England unsatisfactory and insists that fees are generally too high, and that the scholarship system in vogue in that country does not meet the necessities of the case. He doubts the value of the teaching in the ordinary trade schools and evening classes. More attention to technical research should be required in the universities, and manufacturers should offer more inducements for men to take up chemical technology by better remuneration and opportunity for individual experiment in the works.

PROGRESS IN THE CHEMICAL INDUSTRIES.—Moulton (*J. Soc. Chem. Ind.*, **1904**, 1063) considers the trend of invention in chemical industry under three heads: (1) The products; (2) the sources of material; (3) the processes of chemical industry. Concerning

new products, he finds many special ones are being introduced to meet peculiar and unusual requirements, especially in explosives and in the coal-tar products industries. Artificial indigo is instanced as making rapid advances and seriously threatening the natural dyestuff. Pharmaceutical products are especially prominent at present among the newer chemical manufactures, and it is predicted that rapid advances in discovery and technology of new drugs may be expected in the near future. The production of synthetic or artificial foodstuffs is another actively growing field of industry. Preservatives of food articles and the conversion of waste materials into forms capable of assimilation are the two chief lines along which advances in these industries are looked for. The difficulties connected with the use of preservatives are very great, and as yet have not been overcome, but there is good prospect of advance in this direction. Little change is likely to occur in the demands upon the sulphuric acid and alkali industries, but the production of cyanides is rapidly extending and the old methods of manufacture are giving way to new processes. Concerning new sources of material, industrial uses for atmospheric nitrogen seem to be a very promising field for investigation; at present only combined nitrogen is of much importance, and the extended use of internal combustion engines is looked upon as giving impetus to the processes which yield ammonia as a by-product in the making of gas for such engines, and to the recovery of nitrogen from the waste products of the combustion. The work of Dr. Mond along these lines is cited as great and far-reaching in its character. In this same connection are to be grouped the efforts to utilize peat and recover its nitrogen content. The utilization of bacteria as a means of fixing atmospheric nitrogen is one of the most recent lines of advance. Preference will be given hereafter to large sources of comparatively low-grade materials, depending upon improvement in plants and increase of skill for economical production. Large scale operations are characteristic of the newer developments in industrial chemistry. In the processes employed most new inventions are in the direction of increasing yields or of utilizing new by-products. Much importance is attributed to "slight variations in surrounding circumstances" as affecting the increase or failure of manufacturing processes; inventors and investigators must give attention to rendering more certain and complete the reactions and processes which are now uncertain, owing to unknown reactions taking place, or to progressive increase of unsuitable reactions. Certainty and uniformity of conditions throughout the process are essential. Comparisons drawn from various industries illustrate this point. The author expresses disappointment at the slow advance of electrochemical reactions in organic chemical manufacturing. The electric furnace is, however, becoming the basis of important industries; it

is especially adaptable to endothermic reactions, and the heat can be directly concentrated where desired and readily controlled. The step from the discovery of a process to its commercial utilization is often very difficult, and frequently takes rank of itself as an invention. A lengthy and interesting discussion of the paper followed.

METALLURGY.—Beilby (*Electrochem. and Metall., 1904* (3), 806) has "a new theory of the hardening of metals by plastic flow." He finds two distinct solid phases—the hardened or amorphous, called the A phase; and the annealed or crystalline, called the C phase. The A phase passes into the C phase by the agency of heat, and the C phase passes into the A phase by mechanical flow. Between these are two intermediate mobile phases called M and M′. The facts upon which this theory is based are: (1) Very distinct mechanical properties in the phases A and C; (2) the microstructure in the several phases; (3) the optical properties of the phases A and C; (4) the electrical properties of these phases; (5) the thermochemical properties of the phases A and C. The several phases were studied by silver in the metallic state, the properties of which are enlarged upon. Application of the theory is made to certain conditions in the operation of wire drawing, rolling and hammering. Gray (*Electrochem. and Metall., 1904* (3), 501) has investigated the cause of certain explosions of casks of ferrosilicon, which had stood on a wharf for several weeks. As only 0.1 per cent. of calcium was present in the alloy it did not seem probable that calcium carbide could have caused the trouble; but considerable amounts of phosphorus and arsenic were found, and also hydrides of these elements were in the gases in the casks; hence the author thinks these gases may have caused the explosion. Dupré and Lloyd (*Iron and Steel Inst.*, May 5, 1904) investigated the same explosions and found that the powdered material liberated a gas when wet, consisting mainly of hydrogen phosphide, which, with air, formed an explosive mixture. Explosion probably resulted from friction between the lumps, or from spontaneous ignition of the phosphoretted hydrogen liberated from a cavity in a lump, through fracture. It is suggested that the drums be filled in with paraffin oil of high-flash test. Gin (French Patent No. 334132, 1903) proposes to manufacture aluminum by reducing aluminum chloride with sodium-zinc alloy. The sodium-zinc chloride produced is used in the fused state as electrolyte to regenerate the sodium-zinc alloy. Wust (*Stahl u. Eisen*, 1904, (24) 28) publishes the results of experiments in a large way with varying quantities of limestone in the charge for a cupola furnace. The total amount of metal melted in each case was from 15,000 to 20,000 kilos, and eleven runs were made. The proportions of the charge were: 500 kilos of pig iron, 30 kilos of coke, and limestone varying from none to 10 kilos. The limestone was supposed to slag

the ash of the coke and carry some of the sulphur of the fuel into the slag. Increase of limestone to about 9 kilos reduced the sulphur in the metal nearly one-half; no special effect on the phosphorus and manganese was observed; the silicon varied irregularly. In the slag the lime content, of course, increased, but the manganese and iron decreased a little; the alumina fluctuated much, and this was attributed to action on the furnace lining. The silica, in general, decreased, but in a few exceptions a rise took place. The sulphur varied much, and apparently without connection with the amount of limestone used. It is suggested that the amount of sulphur in the slag is influenced by the temperature and viscosity of the fused slag itself. The mechanical loss of iron, manganese and silicon in the slag increased with the increase of limestone, but was generally less than is commonly supposed, being only about 1.6 per cent. in the highest total. The metal attains an increased resistance to shock and in tensile strength, and becomes stiffer as the limestone charge is increased, up to 6 or 8 kilos. Surzycki (*Stahl u. Eisen*, 1904 (24), 163) describes the making of open-hearth steel in a continuous furnace, as worked in Russian Poland. The furnace, holding about 50 tons, is provided with two tap-holes, one higher than the other, through which about one-half of the contents of the furnace can be drawn off, leaving a large bath of molten metal on the hearth, into which the next charge is poured. Lime is used to dephosphorize the metal, and during the tapping ferromanganese and charcoal are added in the ladle. These cause a vigorous reaction, which is soon over, and the metal is ready to cast into ingots. After a ten-day or two weeks' run in this way the lower tap-hole is opened and the hearth emptied; the cycle of operations is then repeated. D. Baker (*Iron and Steel Metall.*, 1904 (7), 21) states that the Otto-Hoffman coke-oven gas was found unsuited to use in the open-hearth furnace, but by injecting some coke-oven tar along with the gas, or by using tar alone, very good heat was obtained. About one pound of tar was equivalent to 12.52 feet of gas, but 1,952 pounds of tar were necessary to equal 1,076 pounds of coal, used to furnish producer gas. The sulphur introduced from the coal was, however, much in excess of that from the coke-oven gas and tar. Cowper-Coles (*Electrochem. and Metall.*, 1904 (3), 828) has a new method of protecting iron and steel from corrosion by heating it to 500°-600° C., while enclosed in an air-tight receptacle, which is coated with graphite and filled with zinc-dust. The thickness of the zinc coat depends on the temperature and the time of heating. This new method of dry galvanizing is called Sherardizing. It is claimed that the whole of the zinc-dust is utilized and that the iron is not materially weakened, as in the case of the fused zinc-bath, and as the temperature is about 200° lower the temper of steel wire and similar forms is not reduced. Illustrations of the apparatus accompany the

paper. Copper is claimed to be case-hardened by the process. Leo (*Chem. Ztg.*, 1904 (28)) describes the Monell process of steel-making. It is a modified Martin basic process, taking melted iron direct from the blast-furnace and mixing it with limestone and iron ore. The phosphorus, silicon and manganese go into the slag, leaving the steel nearly free. More ore is added and the metal further heated until the carburization is at the proper point. Berthelot (*Compt. Rend.*, 1904 (138), 1153) has calculated the melting temperature for gold, using formulae which he has worked out, and applying them to the data of Holborn and Day, Jacquerod and Perrot and himself. The figures are 1064.3°, 1067.4° and 1065.6° respectively. Collins (*Trans. Inst. of Min. and Metal.*, 1903) gives a long and complete review of the methods for wet amalgamation of silver ores in Mexico. Kellermann (*Ztschr. Berg. u. Hüttenw.*, **51**, 606) ascribes the cause of difficulties in roasting zinc blende to the formation of basic zinc sulphate, which, when reduced, yields zinc sulphide and oxide besides metallic zinc. The utilization of the sulphur dioxide in the lead chambers is hindered by the presence of fire-gases and smoke from the furnace. These difficulties could be avoided by using muffle furnaces with hearths one over another, and excluding the fire-gases; each hearth should have an independent air supply to oxidize the blende and burn the sulphur, and the sulphur dioxide should be rapidly drawn out through special outlets. By blowing steam into the lowest hearth, especially at the end of the process, better results are obtained.

FUEL.—Doane (*Eng. News*, 1904 (52), 141) has published some observations upon the spontaneous ignition of coal. The danger of spontaneous combustion is largely dependent upon the quantity of moisture in the coal; for a bituminous coal more than 4.75 per cent. of moisture is unsafe. Iron- or steel-covered bins are recommended, and a free passage of air around all sides and under the bin is desirable, but air-chambers through the mass of the coal are condemned as increasing the risk of rapid oxidation. Cracks and open joints in the bins also admit air to the coal with consequent danger. The depth of coal in the bin should not be more than 12 feet in any case.

ELECTRIC FURNACE PRODUCTS.—Minet (*Electrochem. Ztg.*, 1903) describes the development and uses of electric furnaces, and gives a long bibliography upon them. A French patent (No. 334684, 1903), taken by the *Chemische-Fabrik. Greisheim-Electron*, claims the manufacture of electrodes for electrolytic cells by fusing pyrite cinders or iron oxide in an electric furnace and then casting the fused mass in molds. They are said to have very good conductivity. The same company has taken out another French patent (No. 334685) for the electrolytic production of bichromate from a chromate solution, which is placed in both anode and cathode compartments, and separated by dia-

phragms. Lead anodes and iron cathodes are used. Neuberger (*Ztschr. angew. Chem.*, 1904 (17), 104, 129) reviews the patents taken for the manufacture of iron and steel by use of the electric furnace. A description of the Neuburger-Minet furnace, with drawings, is included. The advantages of the electrolytic process are: (*a*) A more uniform and solid steel; (*b*) different qualities of steel can be made in the same works, with no loss of time in starting or closing out; (*c*) decreased cost of furnace construction; (*d*) repairs can be made without stopping the plant, for several reserve furnaces can be rapidly put into operation; (*e*) interruptions to the working of the furnace are less liable to happen than with the Bessemer or open-hearth plant. Ditz (*Chem. Ztg.*, 1904 (28), 167) reviews the formation of graphite by separation of carbon from carbides. The reaction $CaO+3C=CaC_2+CO$ is reversible at about 1620° C., and Frank has utilized this to make crystalline or amorphous carbon from calcium carbide. The graphite made by Acheson from coal contains from 10 per cent. down of ash; it cannot be made from the carbon in the charge merely by the heat of the furnace. The presence of the ash in the coal is essential to the graphite formation; it has been recently suggested that the mineral constituents of the coal may act as catalytic substances to cause decomposition of the carbide first formed. Acheson has found that metallic oxides or sulphides in the charge assist the process, but as these are not in the finished graphite the author supposes that carbon monoxide causes the decomposition of the carbides formed from the amorphous carbon, and the oxides of silicon, calcium, aluminum, etc., of the ash. In time the temperature rises to a degree at which more or less of the oxides themselves vaporize, leaving the graphite more or less pure. Dissociation of the carbides also causes the formation of crystalline carbon. The author also considers the reaction between calcium carbide or acetylene and carbon disulphide and various organic sulphides as promising future methods of removing sulphur from oils, benzene and, perhaps, coal-gas. Free carbon and calcium pentasulphide and hydrogen sulphide are formed in these reactions, which were observed by Sandmann. Moissan and Hoffmann (*Ber. d. chem. Ges.*, 1904 (37), 3324) have prepared a molybdenum carbide by electrically heating a mixture of molybdenum, aluminum and petroleum coke in covered crucibles. Its formula is given as MoC, and it is a grayish crystalline powder.

ELECTROLYSIS AND ELECTROCHEMISTRY.—Steiner (*Ztschr. Elektrochem.*, 1904 (10), 317) has studied the conditions of working in the "bell process" for electrolysis of salt. The process depends upon the addition of fresh brine to the anode compartment and upon the effect of increased density in the caustic liquor to affect separation of the anode and cathode products; no diaphragm is used. It is highly essential that the brine solution be fed to

the anode compartment in such a way as to mix with the liquid immediately surrounding the anode, but without flowing into or disturbing the layers of liquid at lower levels. There should thus be found a neutral zone between the caustic liquor of the cathode, and the salt-chlorine solution around the anode. By proper addition of new brine the downward motion of the salt solution prevents the hydroxyl ions from migrating into the anode space, and the neutral zone remains stationary. The weaker the brine and the lower the current density in proportion to the area enclosed by the bell and the greater the concentration in the cathode liquor the higher will the neutral zone stand in the bell, and hence the nearer it is to the anode. In general, this zone should not be less than 1 cm. below the anode. A lye of 120 to 130 grams potassium hydroxide per liter can be made continuously in large works, with current efficiencies of 85 to 94 per cent., using a current of 2 to 4 amperes per square decimeter of bell area and 3.7 to 4.2 volts; there was above 97 per cent. chlorine in the anode gases. Ordinary carbon electrodes yielded colored products, but Acheson graphite worked well. In the *Electrochemist and Metallurgist*, 1904, 837, appears a description of the Hazard-Flamand process for electrolytic oxygen and hydrogen, with diagrams and descriptions of the apparatus and various data from a works operating at Petit St. Vrain, near Paris. The electrolyte is a 15 per cent. caustic soda solution in distilled water. With an electromotive force of 2.1 volts and a current of 242 amperes per cell the yield is 1.8 cubic feet of oxygen per hour and 3.6 cubic feet of hydrogen. The actual working voltage is, however, nearer 2.4 volts. Müller (*Ztschr. Elektrochem.*, 1904 (10), 776) finds that the addition of hydrofluoric acid in place of some of the free sulphuric acid gives an increased yield in the preparation of persulphates. No crusts of persulphate should be permitted to deposit on the anode. Müller (*Ztschr. Elektrochem.*, 1903(9), 978) also found on electrolyzing hot concentrated solutions of nitrates at a current density of 0.5 to 1 ampere per square decimeter that nitrites are produced. At first the current efficiency is about 85 to 92 per cent., but decreases as the amount of nitrite produced increases, owing to the formation of ammonia. With 50 to 60 per cent. yield of nitrite the efficiency is only 40 per cent. Köller and Askenasy (English Patent No. 23151, 1903) have a method of improving the circulation of the electrolyte by introducing the electrolyte from the side of the anode and causing it to flow in a zigzag path to the cathode compartment, between certain wedge-shaped parts of the diaphragm, the flow of the electrolyte being at right angles to the lines of electrical force and to the direction of diffusion in the diaphragm. Kellner (English Patent No. 20889, 1903) proposes to introduce a hot 22 per cent. solution of salt into the anode compartment and cause it to pass through the diaphragm

as a filter in the bottom of the anode chamber. By suction on the cathode chamber, or by maintaining a higher level of liquid in the anode compartment, the flow of the electrolyte is secured. The asbestos diaphragm is covered with powdered barium sulphate and the flow of the electrolyte is regulated so that it passes the filter-diaphragm at a slightly greater speed than the velocity of the hydroxyl ions moving towards the anode chamber. Elbs and Becker (*Ztschr. Elektrochem.*, 1904 (10), 361) have electrolyzed bisulphites according to the reaction $2NaHSO_3 + 2H = Na_2S_2O_4 + 2H_2O$. The process seems favorable for dilute solutions, but with concentrated liquors there is a formation of thiosulphate, $Na_2S_2O_4 + 2H = Na_2S_2O_3 + H_2O$. It is, however, proposed to use the process by direct electrolysis in the indigo vats, since here the hydrosulphite, as soon as formed, at once reduces some indigo and is again regenerated at the cathode. Freund (*Ztschr. angew. Chem.*, 1904 (17), 45) describes a graphite-like mass, taken from the iron water-pipes near an electric road in Frankfurt-on-the-Main. Analysis showed the substance to contain free iron, 10.4 per cent.; ferrous silicate, 44 per cent.; ferrous phosphate ($Fe_3P_2O_8$), 37.1 per cent.; carbon, 8.1 per cent. The phosphoric acid and silica originated in the phosphorus and silicon in the iron. An experiment proved the deposit to be the result of electrolytic action. Gray (*Sitzungsber. Kgl. pr. Akad. Wiss.*, Berlin, 1903, 1016) has studied the ozone production by the silent discharge in a Siemens apparatus. The yield of ozone per coulomb is constant for each apparatus and is not affected by potential differences between the electrodes; hence the best yield is had when the potential difference will just cause the luminous discharge in the apparatus while passing gas through it. Warburg, by subjecting oxygen to the silent discharge from a point electrode, found that a decreased yield of ozone per coulomb resulted from increased current strength, if the electrode potential was negative; when positive, an increase of current strength gave a larger yield of ozone per coulomb. A discharge between dielectric surfaces yielded four or five times as much ozone per coulomb as with point electrodes. Siemens & Halske Co. have patented in France (No.335453) a method for the electric production of nitrogen oxides by passing a mixture of oxygen and nitrogen, under several atmospheres pressure, through an electric arc and then passing to absorbers. The mixture then goes through cooling and absorbing apparatus. Benier, in a French patent, proposes to separate oxygen from the air by utilizing its magnetism. An iron or steel drum rotates between electromagnets by which its peripheral surface is magnetized and accumulates oxygen, which is continuously rubbed off into a receiver by a fixed appliance. Namias (*Monit. Scient.*, (18) 487) gives the composition of baths for depositing nickel, copper, silver, gold, brass, platinum and iron. Von Lepel (*Ber. d. chem. Ges.*, 1904 (37),

712) has studied the yield of nitrogen oxides obtained from air by the flame discharge between a copper wire anode and a carbon cathode. The gases from near the cathode contain relatively more nitric oxide than those near the anode, but at greater distances the conditions are reversed. The formation of nitrogen oxides is ascribed to electrical action rather than to the temperature. The temperature of the air at a fixed distance from the flame increased as the rotation speed of the anode increased (the voltage and amperes remaining constant in the primary circuit); the yield of oxide increased with the temperature up to a maximum, but medium temperature and frequency gave the best yield. Soaking the cathode in caustic potash or copper sulphate improved the yield. By passing the nitrous gases into alkali carbonate solution a mixture of nitrite and nitrate of sodium is obtained, suitable for fertilizer; conversion of the nitrite to nitrate is not necessary for this use. Haber and Brauner (*Ztschr. Elektrochem.*, 1904 (10), 697) have made a careful study of the carbon cell, and the reactions in it between the carbon, iron and fused caustic soda. They show that it is not a primary cell, but is properly an oxygen-hydrogen gas cell. The oxygen is derived from the air by the iron electrode, which becomes passive in the fused caustic and thus acts as an oxygen electrode. The carbon reacts with the fused caustic to form sodium carbonate, while hydrogen is evolved, thus producing the current. After extended careful measurements of potential at the two electrodes the authors concluded that the cell gives little promise of commercial utility. Friessner (*Ztschr. Elektrochem.*, 1904 (10), 265) finds that alkali sulphites, subjected to electrolytic oxidation in neutral solution, yield sulphate and dithionate at the anode. Acid solutions do not react thus, but form hydrosulphite and thiosulphate at the cathode. A high potential at the anode, especially if accompanied by a rise of temperature, is favorable to the formation of dithionate, but high current density retards the process. Fontana and Perkin (*Electrochem. and Metal.*, 1904 (3), 656) have studied the electrolytic oxidation of anthracene. Owing to the relative insolubility of anthracene in water and other liquids, an emulsion of it in 20 to 30 per cent. sulphuric acid was tried; the amount of oxidation was very small, both in cold and in hot suspensions. Then a mixture of a solution of anthracene in acetone, with dilute sulphuric acid, was electrolyzed in the anode compartment, using platinum electrodes. On standing over night, after the electrolysis, anthraquinone crystals were obtained. Oxidation in alkaline solution resulted in some anthraquinone formation, but the yield was not so good as in acid liquors. Agitation of the electrolyte improved the oxidation in all cases. In the acetone electrolyte, only 50 to 55 per cent. of the anthracene could be oxidized. Petroleum and pyridine solvents gave unsatisfactory results. The addition of oxygen-carry-

ing substances, such as salts of chromium, magnesium and cerium, in acid solution, accelerated the oxidation, but the highest yield of anthraquinone was only about 80 per cent. The solutions were kept at near 75° C.; higher temperatures caused excessive frothing. By using a relatively small cathode surface, and a large anode, the diaphragm could be omitted, and the results remain about the same. The cathode was rotated rapidly, and served to stir the cell contents. The current density used was 1 ampere per square decimeter at the anode, and at the cathode it was 12 amperes; the voltage was 2.9 to 3.5. It is concluded that in large works, no diaphragm would be satisfactory, since the migration of the sulphate ions into the cathode space, would increase the acid concentration at the anode, while the cathode liquor loses strength. Reference is made to the German patent (No. 729502), of Moest, for the electrolytic oxidation of anthracene, using cerium salts as an oxygen carrier. Current density of 5 amperes per square decimeter, at 2.9 to 3.5 volts, is used. Möller (*Elektrochem. Ztg.* (10), 199) has reduced nitro-compounds of the naphthalene, anthracene, and phenanthrene series by electrolysis. It appears that the nitro bodies are reduced to amino compounds at once, and no intermediate products were found.

ACIDS, SALTS, ETC.—Taylor (*Lit. and Phil. Soc., Manchester,* Jan., 1904) describes a method for making hydrobromic acid in a large way. A bromide is mixed with some amorphous phosphorus and a little water. Concentrated sulphuric acid is added and heat applied. The hydrobromic acid is evolved free from bromine, but containing traces of sulphurous acid. Spence and Craig have patented (English Patent Nos. 2211 and 2223, 1903) a method for recovery of bichromates from waste liquors containing ammonium chromate. The solution is treated with lime to precipitate calcium chromate and set free ammonia, which is recovered. The calcium chromate is suspended in a solution of potassium carbonate, and ammonia and carbon dioxide passed in.

The mixture of ammonium and potassium chromates is boiled until the ammonia is driven out, and potassium bichromate results. Lebeau (*Compt. Rend.*, 1903 (137), 1255) has studied the dissociation of alkali-metal carbonates, and finds that all of them dissociate when heated *in vacuo* to 800° C.; the resulting oxides are volatile at this temperature. Lithium carbonate appears to dissociate more readily than sodium carbonate, but caesium and rubidium carbonates dissociate more easily than potassium carbonate. Bauer (*Chem. Ztg.*, 1903 (27), 1268) describes the modifications which were necessary in the process of separating potassium chloride from a mixture of carnallite, sylvine, and so-called "Hartsalz," when the works attempted to use "Hartsalz" alone, and when mixed with other salts. The usual solvent was mother-liquors from previous crystallizations containing common salt and potassium chloride. This solution, agitated and heated with raw

materials until the concentrated solution reaches 1.3 specific gravity, is then settled, decanted and cooled to crystallize. The crystals test about 84 per cent. potassium chloride. Heating by steam coils is recommended because of the more exact control possible. Witt and Ludwig (*Ber. d. chem. Ges.*, 1903 (36), 4384) have found that barium nitrite can be made from sodium nitrite and barium chloride with nearly 85 per cent. of a theoretical yield of twice crystallized salt. On large scale work, the yield would undoubtedly be much better. An excess of 100 per cent. of sodium nitrite over the theory is used, which caused the sodium chloride to "salt out" of the solution, since the salts have a common ion. The mixed sodium nitrite and barium chloride are run into a boiling solution of an equal weight of sodium nitrite; the sodium chloride is filtered from the hot liquor, and the filtrate, on cooling, deposits crystals of barium nitrite; the mother-liquor is boiled again and a new charge of salts introduced. Barium nitrite is stable up to 115° C., and is used for diazotizing amines in sulphuric acid solutions, whereby the filtered solution of the diazotized compound, is free from inorganic salts. It can also be used to form other metallic nitrites by double decomposition with sulphates. The process seems to be promising as a commercial method of preparation. Hardwick (*J. Soc. Chem. Ind.*, 1904, 218) describes a professional experience in dealing with a sulphuric acid plant which had gotten into "difficulties," owing to the large amount of arsenic in the ore. So much arsenious oxide was formed that the tower acid became saturated with it and the Gay-Lussac tower became clogged, owing to its separation through the filtering action of the coke. The hotter and stronger the acid, the more arsenious oxide it dissolves in the Glover tower. The remedy finally adopted was oxidation to arsenic oxide by treatment with nitric acid, $As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3$. The arsenic oxide being more soluble in sulphuric acid, did not separate; the nitrogen trioxide remains dissolved in the strong acid and is recovered. Details of the working of the method are given. The arsenic oxide remained in the acid, as an arsenic-free product was not required, but merely that a highly arsenical ore should be utilized. Küster (*Chem. Ztg.*, 1904 (28) 132) gives some results upon a study of the hydrates of nitric acid. By a study of freezing-points of acid of increasing strengths, two maxima were observed, corresponding to $HNO_3.3H_2O$ and $HNO_3.H_2O$; also three minima. These hydrates were obtained as solids and as liquids; the monohydrate is the less stable of the two. Carpenter and Linder (*J. Soc. Chem. Ind.*, 1904, 577) have continued their study of the Claus reaction in plants connected with gas-works, giving particular attention to the sulphur loss. Complete details of numerous tests upon inlet and exit gases from the kiln, the amount of ammonium salts in the recovered sulphur, and the effect of cyanogen compounds in the gases in the production of the ammonia are all

considered. The article does not admit of a satisfactory short abstract. Inglis (*J. Soc. Chem. Ind.*, 1904, 643) has attempted to trace the loss of niter in the chamber process by subjecting the exit flue gases to fractionation from the liquefied gases at low temperature. The flue gases may contain nitrogen, oxygen, nitric oxide, nitrogen peroxide, nitrous oxide, sulphur dioxide and vapors of sulphuric acid. By cooling to —185° C., in a spiral worm, it was found that these gases, except the nitrogen and oxygen, became non-volatile solids, although the nitric oxide still has a slight vapor pressure and could not be completely separated from the nitrogen. By fractionation at proper temperatures the several solids were separated into the groups: (1) nitrogen and nitric oxide; (2) nitrous oxide and carbon dioxide; (3) sulphur dioxide; (4) nitrogen peroxide and sulphuric acid. These were then analyzed. The total volume of flue gas examined was 284 liters. About 0.002 per cent. of nitrous oxide was found in each trial; sulphur dioxide amounted to 0.02 per cent., if the gases had been washed with oil of vitriol; otherwise none was found; about 0.02 per cent. nitric oxide was present, but this was not exact owing to the vapor-pressure. Assuming this loss to be equal to the quantity found, the total amount of nitric oxide in the flue gases was 0.04 per cent., carbon dioxide, 0.05 per cent., and sulphuric acid about 0.008 gram per liter of gases. Nitrogen peroxide is difficult to estimate, as it acts on mercury, and had to be determined by difference; it was determined as about 0.03 per cent. of the flue gases. Taking the total of the nitrogen peroxide and nitric oxide they amount to 0.07 per cent. of the gases, but the total loss of niter in the system (about 3 per cent. of that used) represents only 0.1 per cent. in the exit gases, hence it is concluded that the loss is due to inefficient action of the Gay-Lussac tower, and may be considered a mechanical loss. In the report of the chief inspector of alkali works for 1903, it is stated that the bottom inlet for vitriol chambers, described by Porter (*J. Soc. Chem. Ind.*, 1903, 477), has been tried in several works, one showing a 7 per cent. increase of yield of acid, and a decrease of niter consumption equal to 1 per cent. A method of utilizing the waste arsenic sulphide mud from the purification of sulphuric acid is much to be desired. Trautz (*Ztschr. physik. Chem.*, 1904 (47), 513) has published a very long and detailed investigation upon the physical chemistry of the lead chamber process for sulphuric acid. A very complete bibliography of previous investigations on the process is given and some of the unsolved problems are stated When an indifferent gas is passed through solutions of nitrosulphonic acid, in different concentrations of sulphuric acid and water, the sulphonic acid decomposes more quickly in the more dilute acid, at temperatures of 25° C.; a mixture of nitric oxide and nitrogen peroxide is evolved, the amount of the latter being greater

with the more concentrated sulphuric acid solutions. The hydrolysis of the nitrosulphonic acid in concentrated sulphuric acid was measured, but in the dilute solutions the speed of hydrolysis was too rapid for accurate measurement. The following reactions are proposed as representing what takes place in the lead chambers: (1) $2NO_2.SO_3H + 3SO_2 + 2H_2O = 2NO(SO_3H)_2 + H_2SO_4$; (2) $NO(SO_3H)_2 + 2NO_2.SO_3H + 2H_2O = 3NO + 4H_2SO_4$; (3) $2NO + O_2 = 2NO_2$. The author considers Raschig's theory as the most satisfactory, but admits that the important reaction (I) and the compound $NO(SO_3H)_2$, nitric oxide disulphonic acid, have not been observed in practical working. The very elaborate and extended series of experiments carried on by the investigator, are not adapted to satisfactory condensed abstraction. Raschig (*Ztschr. angew. Chem.* 1904 (17) 1398) publishes a long explanation of his theory of the chamber process. From a study of the reactions between nitrites and bisulphites, and of nitrous acid on sulphurous acid, the author published, many years ago, certain equations as expressing the chamber reactions, as follows: (1) $ON.OH + H.SO_2.OH = ON.SO_2.OH + H_2O$; (2) $ON.SO_2.OH + ON.OH = SO_2(OH)_2 + 2NO$; (3) $2NO + O + OH_2 = 2(ON.OH)$. From his more recent studies of the question, he regards these as confirmed, but admits some uncertainty as to the second; it is possible that the nitrososulphonic acid may not be oxidized directly to sulphuric acid and nitric oxide but some pernitric acid may be formed, thus: $ON.SO_2.OH + 6(ON.OH) = 6NO + H_2SO_4 + HNO_4 + 2H_2O$. Since this is very unstable, it decomposes at once into nitric acid and nitrogen peroxide. Divers (*J. Soc. Chem. Ind.*, 1904, 1178) gives an exposition of Raschig's theory of the lead chamber process (see previous abstract). In the discussion of the paper, Professor Tilden considers that the reactions proposed by Raschig have not been proved to be essential to the chamber process. Lunge (*Ztschr. angew. Chem.*, 1904 (17), 1659) replies to the statement of Raschig and Trautz (see above abstracts). He considers the reactions of Raschig to be contrary to all experience, and reasserts that both nitrogen peroxide and nitrosylsulphuric acid are present and necessary in proper chamber work. He holds that Trautz has not given sufficient attention to the discrepancies between Raschig's experiments and the actual chamber conditions. Raschig (*Loc. cit.*, 1777) continues the controversy, but admits Lunge's contention that nitrosylsulphuric acid is present. He maintains that the reactions proposed by himself, are, however, sustained by the facts, as shown by experiment. Kessler has patented an improved cooler for the acid leaving his well-known evaporator, whereby the concentrated acid is brought to a temperature at which it has but little action on lead. At the same time, the acid passing to the evaporator for concentration, is warmed by a heat exchange with the concentrated acid. Lunge and Reinhardt (*Ztschr. angew Chem.*, 1904 (17), 1041) have

continued the investigation upon contact action of ferric oxide and admixtures of it, with other substances, for the production of sulphur trioxide, which was instituted by Lunge and Pollitt (*Ztschr. angew. Chem.*, 1902 (15), 1105). The tube containing the contact mass was heated in an electric resistance furnace, in which close observation of temperature was possible. The influence of temperature was particularly studied, a Le Chatelier pyrometer being used. With pure ferric oxide (burnt pyrites), the action starts at 400° C., and the maximum is reached at 625° C., with about 70 per cent. of the sulphur dioxide converted. No effect was noticed when the gases were dried over phosphorus pentoxide and the addition of arsenic trioxide did not appear to increase the conversion over that obtained with pure ferric oxide alone; the results were quite near those of the previous experimenters, with arsenical ferric oxide. A trial with ferric arsenate prepared by precipitation, showed about 70 per cent. conversion of the sulphur dioxide at 625° C., but ferric arsenite gave much lower figures, though there appears to be some doubt as to the purity of this contact mass. About 55 per cent. of conversion was obtained with arsenic pentoxide at 680° C.; cupric oxide alone had even less action, and the admixture of small amounts of copper salts seemed to have no effect. Silica, both as amorphous quartz and as crystal, had a distinct catalyzing effect, amounting to 10 per cent. conversion, at 700° C. Hartmann and Benker (*Ztschr. angew. Chem.*, 1904 (17), 554) criticize certain statements of Meyer, who compares his tangential chambers with the old type of rectangular chambers for sulphuric acid. He claims a yield in his system of 5 kilos of acid per cubic meter of chamber space per twenty-four hours, corresponding to 7.4 kilos of acid of 1.58 specific gravity (54° Bé.). He puts the corresponding yield of the old process as 2.5 and 3.7 kilos respectively. The authors consider this as abnormally low for well-built, rectangular chambers, and claim that the system must be out of order to produce such a yield. Admitting that Meyer's system requires less lead, they assert that it costs more to erect and keep in repair, and that certain kinds of repairs can only be made by practically shutting down the system. They claim that the tangential circulation is not ideal, that dead spaces exist in the system, and the reactions are not complete. A French patent (No. 335496) claims the manufacture of hydrochloric and sulphuric acids by bringing chlorine, sulphur dioxide, and water in contact, in proper proportions and under suitable control. Hydrochloric acid gas and liquid sulphuric acid are the products. With excess of chlorine, the hydrochloric acid is nearly free from sulphuric acid.

GAS AND ILLUMINATION.—King (*J. Gas. Lighting*, 1904 (85) 80) describes some experimental vertical retorts in use at Exeter, Eng. The retorts, improvised from 16-inch circular retorts,

have on the top a short tube 6 inches in diameter, in which a rod, carrying two conical plungers, with apices pointing upwards, is worked up and down by automatic gearing. As the top cone rises out of the tube on the up-stroke, fine coal slack runs into the tube on top of the lower cone. On the down-stroke the lower cone passes below the tube and into the retort, the coal resting on it dropping into the retort, the upper cone having again passed into the tube and cut off the feed of fine coal. Thus the coal is fed into the retort continuously, in regulated charges of about 6.5 pounds each. No loss of smoke or flame takes place during charging, and the claim is that over 13,000 cubic feet of gas are obtained per ton of coal, as against 10,000 cubic feet from the horizontal type of retort. A saving of floor area and brickwork, with a lower temperature of carbonizing and a more uniform quality of gas, are the chief points claimed. Patterson (*J. Gas Lighting*, 1904 (87), 606) has investigated the effect of barometric pressure and the humidity of the air upon the candle-power of the Harcourt pentane lamp. Two electric lamps of the Fleming-Ediswan type were used as standards, and the pentane lamp was compared photometrically with these under varying atmospheric conditions. Assuming 10 liters of water vapor per 1000 liters of air and barometric pressure of 760 mm. as normal, a correction formula for the 10-candle-power lamp was deduced, thus :

$$C.\ P. = 10 + 0.066\ (10 - \epsilon) - 0.008\ (760 - b),$$

when ϵ = the humidity and b the barometric height in millimeters. From this it can be shown that variations of 1 liter of water vapor per cubic meter influence the candle-power 0.7 per cent., and 10 mm. fluctuation of barometric pressure affects the luminosity of the lamp about 0.8 per cent. Haber and Richardt (*J. Gasbeleucht.*, 1904 (47), 809, 833, 864, 877) have analyzed the gases from the inner cone of the Bunsen flame. The water-gas equilibrium $CO + H_2O \rightleftarrows CO_2 + H_2$ was found to prevail there. The thermoelectric determinations of the temperature of the inner combustion zone were practically the same as those calculated from the composition of the combustion products, using the reaction-isochrore of the water-gas equilibrium. Erdmann and Bedford (*Ber. d. chem. Ges.*, 1904 (37), 1184) prepared pure oxygen by the action of hydrogen peroxide on potassium bichromate in a Kipp apparatus. It was then subjected to cooling by liquid air, suitable precautions being taken to exclude air from the oxygen. The liquid oxygen analyzed 99.8 per cent. oxygen, and the boiling-point was found constant at —181.8° C. The liquid absorbs nitrogen to a large extent, taking up at —190.5° C. some 380 volumes of gaseous nitrogen, or 42 per cent. of its weight, and at —191.5° C. 460 volumes, or 50 per cent. was absorbed. It thus appears impossible that pure oxygen could be made from

liquid air by fractional evaporation. Stock (*Ber. d. chem. Ges.* (37) 1432) refers to the above observations as merely a case of two miscible liquids, and no chemical relation between the substances is shown. Hache has taken a patent in France (No. 334783, 1903) for a carburetted alcohol, produced by mixing denaturated alcohol with crude petroleum in equal volumes and then distilling off the alcohol. A homogeneous distillate is obtained which has much more luminosity than ordinary alcohol and which does not form noxious vapors, nor leave greasy residues. The material is presumably used as an illuminating oil, or in gas engines. Bodenstein (*Ztschr. Elektrochem.*, 1904 (10), 123) describes a new form of mercury vapor lamp, devised by Dr. Küch; the apparatus is made of fused quartz and has the form of an **H**-tube, with iridium electrodes fused into the vertical tubes. The arm connecting the two vertical tubes is 17 cm. long and slightly inclined. By electrically heating one of the side tubes the mercury vaporizes and the vapor forces the liquid mercury along the connecting tube to the other side tube, making a short circuit. At the moment of contact the heating current is mechanically cut off and the liquid mercury draws back into the vertical tube and the arc begins to burn at once. A current of two amperes at 100 volts is used between the two mercury surfaces. The brilliancy is about equal to that of a carbon arc light, and the color is greenish but the light is rich in ultraviolet rays. A strong odor of ozone was noticeable at the beginning of the lamp's operation, but this disappeared as soon as the tubes became hot, the ozone being thus destroyed. Paweck (*Ztschr. Elektrochem.*, 1904 (10), 297) has proposed a new kind of mercury-vapor lamp, in which the lamp is started by having the electrodes connected by mercury before starting and causing them to be separated by throwing the mercury to each end of the horizontal tube by centrifugal force, developed by rotating the lamp when it is in action. Gardner and Dufton (*J. Soc. Chem. Ind.*, 1904, 598) have devised a new lamp (the "dalite") for color-matching. It is an arc lamp, surrounded by a special glass which absorbs those rays from the lamp which are in excess of normal hues present in daylight.

CYANIDES.—Feld (*J. Gasbeleucht.*, 1904 (47), 132, 157, 179), in a study of the Bueb's process for cyanogen recovery, finds that the cyanide mud contains only one-fourth of the insoluble double ammonium-ferrous-ferrocyanide, one-fourth insoluble iron cyanide and one-half as soluble ammonium ferrocyanide. There is trouble in recovering the ammonia, and the working of the cyanide mud is not adapted to gas-works routine. The author recommends using an 18 per cent. copperas solution, which is dilute enough to work easily and yet retain the cyanogen as ammonium salt. Körting (*J. Gasbeleucht.*, 1904 (47), 45) reports upon the working of Bueb's cyanogen recovery process at the Hanover

gas works. After cooling to collect tar and naphthalene the gas passes into a sectional washer containing a ferrous sulphate solution of 20° Bé; the iron is precipitated as ferrous sulphide, which reacts with ammonia and cyanogen to form an insoluble iron-ammonium-cyanide, $2FeS + 6NH_3 + 6CN + 3H_2O + 5O = (NH_4)_2Fe_2(CN)_6 + 2(NH_4)_2SO_4$. This cyanogen mud is pumped out of the washer and collected. It contains about one-third of the ammonia in the gas.

PIGMENTS.—Rohland (*Ztschr. angew. Chem.*, 1904 (17), 609) has investigated the constitution of ultramarine and finds it resembles trass and puzzuloana, has hydraulic properties, and if added to Portland cement increases its binding properties. The soda is thought to be in a condition similar to the free lime in Portland cement. The formula $2Na_2Al_2Si_2O_8.Na_2S_2$ is proposed, but as the substance is isomorphous with the minerals sodalite, hauyn and nosean, it may have the formula $Na_4(Al(NaS_3))(Al_2SiO_4)_3$. The colored constituent is thought to be present in small quantities only, and disseminated through the mass in solid solution. McIntosh (*Chem. News*, 1904 (89), 197) proposes to make Venetian red by heating waste peroxide of lead and anhydrous ferrous sulphate to accomplish the reaction $2FeSO_4 + 2PbO_2 = 2PbSO_4 + Fe_2O_3 + O$. Manganese peroxide may be used and the manganese sulphate recovered. Liebig (*Ztschr. angew. Chem.*, 1904 (17), 157 *et seq.*) has a series of articles upon the manufacture of white lead by the German (chamber) and French (drum) processes, and the preparation of red lead; details of the processes and tests are given.

CEMENTS.—Gemmell (*J. Soc. Chem. Ind.*, 1904, 306) reviews the methods of Portland cement testing. Uniform methods of chemical analysis are considered unimportant, but uniformity in the physical tests is very essential. The methods of making the usual tests are described. Gary (*Mitt. königl. techn. Versuchsanst.*, 1903 (21) 159) has made tests of the strength of mixtures of blast-furnace slag and binding material. The strength of such mixtures falls rapidly if kept some time. This is more marked with Portland cement mixture than in those made with lime. A decrease in the specific gravity in the test pieces was also noted. The loss of strength is larger proportionally in the resistance to crushing than in the tension strength.

EXPLOSIVES.—Will (*Ber. d. chem. Ges.*, 1904 (37), 268) has a long review of the progress in manufacturing explosives, from the discovery of gunpowder to the present time. Thomson, in a report upon a nitroglycerine explosion at Faversham, Eng., concludes that the dropping of a lead filter into a tray containing about 3 pounds of the explosive caused the explosion of about 1,000 pounds of nitroglycerine in the washing tank. Various precautions for future safety are suggested. The possibility of exploding nitroglycerine by friction of a rubber shoe on a lead

surface was investigated, with negative results; sprinkling sand and powdered sulphur on the nitroglycerine and repeating the trials also gave no explosion. Macnab and Leighton (*J. Soc. Chem. Ind.*, 1904, 293) have studied the products and temperature of combustion of some smokeless powders. The ingredients of a number of commercial powders were determined and then the calories and the composition of the gases were found. The temperatures were taken with the thermoelectric pyrometer of Roberts-Austen, using a rhodium-platinum couple inside of the bomb in which 4 grams of each explosive were fired in the presence of air. The deflection of the galvanometer is directly proportional to the temperature.

GLASS, POTTERY, ETC.—Hertwig (*Sprechsaal.*, 1903 (36), 1845) has experimented on the production of yellow glazes for porcelain. He found that tungsten and molybdenum, in the presence of manganese, gave bright yellow and orange colors when fired in a reducing atmosphere. Manganese peroxide seems to give up oxygen to tungsten at high temperatures, and the color of the glaze becomes reddish yellow or orange. Molybdenum phosphate produced a sulphur-yellow glaze when the biscuit had been treated with manganese chloride. Colloidal tungstic acid yields a range of colors from ivory to orange-yellow after the application of manganese nitrate or chloride, after refiring. Ammonium metatungstate, prepared by heating ammonium tungstate until the evolution of ammonia ceases, furnishes good glaze pigment. Other crystallizable metatungstates, made from nitrates or chlorides, of alkaline earths, or metals, with tungstic acid, can be used in the same way. Certain double salts, made from the alkali metatungstates, by treatment with barium chloride and metallic sulphates, also furnish glaze pigments. Thomason (*J. Soc. Chem. Ind.*, 1904, 469) has examined the extent to which lead oxide volatilizes from the glaze mixture in the glost firing of china and the effect of subsequent volatilization from the walls of the saggar upon the leadless glaze ware in the same saggar. It appears that a leadless glaze may gather from 5 to 6 per cent. of lead oxide in firing. The same author also treats of the preparation of lead glazes of low solubility, the object being the protection of the health of the operatives. The fritt of lead glaze used at the Doulton Pottery is a lead bisilicate containing about 65 per cent. lead oxide and 35 per cent. silica. This is fairly insoluble in hydrochloric acid of 0.25 per cent. (approximate acid strength of the gastric juice). It takes up some alumina in the fritting process and loses some lead oxide by volatilization and absorption in the bed of the kiln. The fineness of grinding of the fritt has considerable influence on the solubility of the lead, but there is no special difficulty in keeping well below the legal limit of 5 per cent. soluble lead oxide. Garros (*Compt. Rend.*, 1904 (139), 68) has devised a new "asbestos porcelain," made

by firing asbestos. The biscuit is quite porous if fired at temperatures not over 1400° C., and is recommended for filters. Above 1650° C. the material fuses to a glass. A mixture of asbestos, with alumina and alkali, if fired at about 1500° C., gives a semivitrified biscuit, very suitable for insulators. A similar mixture, with more alkali and alumina, can be used as a glaze on the biscuit and the insulation is excellent. It is claimed that copper can be fused in with the glaze and attached to the porcelain. Buchner (*Ztschr. angew. Chem.*, 1904 (17), 985) finds that the residue of aluminum oxide from Goldschmidt's alumino-thermal process, when mixed with clay or kaolin for stoneware, gives the pottery great resistance to temperature changes, since it decreases the contraction very much. An increase in tensile strength is also claimed, and the ware is particularly recommended for diaphragms in electrolytic cells. Hopwood (*J. Soc. Chem. Ind.*, 1904, 592) has ignited various clays in atmospheres of nitrogen, carbon dioxide, steam, oxygen, hydrogen, carbon monoxide, ammonia, marsh gas, olefiant gas and air (limited supply and in excess) with special reference to the color produced in the calcined product. He finds that all clays darken when heated alone, or in nitrogen, carbon dioxide or in steam, but they blacken only when organic matter, in moderate or large amounts, is present. The darkening disappears on oxidation; for white, ivory, yellow or red wares, made from clay having little organic matter, but little air is needed to develop their normal color. The darkening is mainly due to carbon, ferrous oxide or magnetic oxide, with occasionally ferrous sulphide and metallic iron. All clays darken in reducing atmospheres, but this is not noticeable unless considerable iron or organic matter is present. The color becomes lighter or redder in oxidizing atmospheres; hence the makers of blue bricks must exclude air from the kiln during the last part of the heating lest a red-brown color develop.

PHOTOGRAPHY.—Baekeland (*Brit. J. Photog.*, 1904 (54), 146) has studied the retrogression of the latent image before development in exposed plates, films, bromide papers and printing papers of the "velox" class. If kept undeveloped for some time after exposure the image may almost entirely disappear. This change is independent of the developer used and is of a chemical nature. At low temperatures (0°-4° C.) plates showed no sensible change after two weeks, but at 40° to 48° C. there was marked retrogression after three days; the change is retarded by keeping the plates in a dry atmosphere over sulphuric acid; presence of acid or chromium salts in the emulsion appear to greatly accelerate the retrogression, but if the emulsion is slightly alkaline retrogression is greatly reduced, even when chrome alum is present. Overexposed plates show little or no change of this kind, but under exposure is especially favorable to it. Retrogression varies considerably with different brands of plates, films and papers, and

is especially marked in certain kinds of films and papers. In another investigation he finds (*Monit. Scient.*, 1904 (18), 355) that slow drying of the emulsion for developing papers containing insoluble silver salts produces more rapid printing and the image is flatter than if more rapidly dried. If soluble silver salts are present in the emulsion, slow drying causes red prints, which are troublesome to tone and soon fade. Rapid drying in dry air at rather low temperature is best. If the air is too dry, the paper becomes electrically charged in passing over the drying machine and attracts dust specks. The same writer (*Loc. cit.*, 362) recommends a pure silver drum for the centrifugal machine used in filtering silver bromide-gelatin emulsion to avoid contamination with other metals. The cover should not be screwed down, as bits of metallic dust wear from the thread and get into the emulsion. A uniform temperature of 30° to 35° C., and uniform and moderate speed are essential; and small and frequent additions of the liquid to be filtered. The bromide is washed in the drum with warm water to remove ammonia, etc. Well prepared silver bromide, kept in a cool place, was found in good condition after two years, being but slightly more sensitive than originally. Witt (*Phot. Mitt.*, 1904 (41), 235) states that pyridine hastens the "ripening" of gelatine silver emulsions without causing granular appearance or fog on the plates. It is proposed to sensitize the emulsion with a double salt, pyridine-silver nitrate, $AgNO_3.(C_5H_5N)_2$. The emulsion, if used without ripening, gives "slow" plates, which give strong contrasts, but by heating to 100° C. for a time the emulsion becomes more rapid and still yields good negatives.

FERTILIZERS.—Wagner (*Illust. landw. Zeit.*, 1903, 959) describes a new fertilizing material, prepared by fusing rock phosphate 100 parts, sodium bisulphate 70 parts, sand 22 parts, calcium carbonate 20 parts, and coal 7 parts. The fused mass is run into water and the resulting sand is ground very fine. The substance is more soluble than basic slag and is almost as rapid in its effect on plants as is superphosphate. It is not hygroscopic and does not deteriorate on keeping in store. It is called *Wolter* phosphate.

VARNISHES, RESINS AND GUMS.—Tixier and Rambaud (French patent No. 334430, 1903) propose to make varnish direct from the gums, without previous melting by solution in "terpeneol," $C_{10}H_{16}O$, a product of the action of dilute nitric acid on oil of turpentine. By digesting turpentine at 20° C., with nitric acid of 20° Bé., crystallizable terpine is formed, which is washed and converted into terpeneol by treatment with dilute sulphuric acid or by distillation with steam. The unmelted gums dissolve in this liquid, or in a mixture of it with turpentine or benzene, to form varnish. For oil varnish a fatty acid which dissolves in the oil is added to prevent precipitation of the gum from the

terpeneol solution by the neutral oil. Collins (*Scientific American*, 1903 (89), 368) reports upon the details of Thurlow's process for artificial camphor, as worked at Port Chester, N. Y. Anhydrous oxalic acid is heated with turpentine oil in steam-heated pans, forming pinyl oxalate and pinyl formate; the liquid product is distilled with steam in the presence of an alkali and the resulting camphor and borneol mixture is filter-pressed, washed to remove oil and then oxidized to convert the borneol to camphor. The crude camphor is then sublimed for further purifying. Forster (*Chem. and Drug.*, 1904 (64), 289) maintains that the bodies called pinyl oxalate and pinyl formate in the Thurlow process for synthetic camphor (see preceding abstract) are bornyl hydrogen oxalate, $C_{10}H_{17}O.CO.COOH$, and bornyl formate, $C_{10}H_{17}O.CHO$, respectively. The former is converted to camphor and the latter to borneol when heated with alkalies, thus: $C_{10}H_{17}O.CO.COOH = C_{10}H_{16}O + H_2O + 2CO_2$; $C_{10}H_{17}O.CHO = C_{10}H_{18}O + CO$. R. G. Smith (*J. Soc. Chem. Ind.*, 1904, 105) publishes a long investigation upon the bacterial origin of vegetable gums. He found that bacteria inhabiting the tissues of the trees can form arabin, metarabin, pararabin and other gums. Differences in the physical nature of gums are ascribed to differences in climate, temperatures of formation and the nature of the tree sap. Differences in season would probably affect the activity of the bacteria and thus cause differences of optical properties; *e. g.*, in the same gums from one season to another. Artificial infection of trees is proposed as a method of making them produce more gum; or, as the author puts it, the world's gum supply might be increased if the natives were taught to "sow bacteria and reap gum."

MISCELLANEOUS.—Thos. Tyrer (*J. Soc. Chem. Ind.*, 1904, 221) has published a long and instructive argument upon the "Need of Duty-free Alcohol for Industrial Purposes." The conditions apply especially to Great Britain, but the facts and figures will apply to this country in many cases. The extended discussion of the paper by many present, throws much light upon the difficulties from the government standpoint. Sisson (*J. Soc. Chem. Ind.*, 1904, 242) describes the production and use of liquefied carbon dioxide. Diagrams of the compressors, coolers, and purifying apparatus, together with the valve for the steel containing flasks, are shown. The gas, after production, is stored in a gasometer, there being a ½-inch layer of mineral oil on the water to prevent absorption of the carbon dioxide by the water. The compression is in three stages: first, to 5 atmospheres, next to 15 atmospheres, and finally to the necessary pressure for liquefaction. The compressed gas passes through water-cooled copper coils, after each compression. The first compression cylinder is lubricated by a small injection of water, which is separated afterwards; the second and third cylinders are lubricated with glycerine, which is also separated by gravity from carbon dioxide. The

steel storage bottles are tested by hydraulic pressure, up to 3360 lbs. per square inch. Valves are made from hard brass or gun-metal. The various uses of the liquid are explained. Marshall (*J. Soc. Chem. Ind.*, 1904, 645), in a paper on acetone manufacture and purification, attributes the deterioration of commercial acetone on keeping, to the presence of certain basic substances similar to methyl amines, not removed in the purifying. It is suggested that the crude acetone be purified by re-distilling over sulphuric acid, instead of caustic soda as now generally done.

OILS, FATS.—T. E. Thorpe (*Proc. Chem. Soc.*, 1904 (19), 12) has examined butters from various sources and finds that the chemical character of the butter-fat is variable and is influenced by the food, breed and peculiar idiosyncracies of the cow, and also by climatic conditions. Nicloux (*Compt. Rend.*, 1904 (138), 1175) finds that the lipolytic substance in castor seeds is the "cytoplasma." It is not yet determined whether this is itself the cause of the hydrolysis of fats, or whether it secretes the ferment. Power and Gornall (*Chem. Soc. Proc.*, 1904 (20), 135) have examined the constituents of chaulmoogra seeds, and find they contain a hydrolytic enzyme and a cyanogen body, which react on each other, and form hydrocyanic acid. The seeds yielded 30.9 per cent. of oil, which had a m. p. 22°-23° C.; sp. gr. 0.951 at 25° and 0.940 at 45° C.; $(\alpha)_D^{15^\circ} = +52$; acid value, 23.9; iodine value, 103.2; saponification value, 213. The oil when saponified yielded glycerol, a little phytosterol, and a mixture of several fatty acids, belonging to the series, $C_nH_{2n-4}O_2$. These have not previously been found in fatty oils. The highest homologue of these acids, in the pure state, forms glistening plates of formula $C_{18}H_{32}O_2$ (m. p. 68° C.); this is called chaulmoogric acid. The press-cake of the seeds yielded an oil, $C_{18}H_{32}O_2$ (b. p. 214° C.), isomeric with the acid. An extended study of this acid was also made, and many derivatives prepared. Hoyer (*Ber. d. chem. Ges.*, 1904 (37), 1436) has continued experiments on the decomposition of fats by enzymes. In germinating seeds, the enzyme near the germ appears weaker than that from the other parts of the seeds; but as germination progresses, the activity of the enzyme decreases. The turbid oil expressed from castor seeds after trituration with sand and cotton oil, induced 81 per cent. of hydrolysis of the latter in three hours. Filtration and removal of turbidity gave an oil without enzyme activity; the residue was highly active. Acidified water was also found suitable for this extraction of the enzyme, but the process does not appear of much value from the technical standpoint. The time of trituration of the castor-seed meal with the oil and with acid water was found to have little influence on the activity. Short, vigorous trituration of the seeds in a paint mill was recommended. The addition of acid appears to be influenced by the quantity of seeds, and a definite amount for each acid tried was found to be necessary;

above a certain maximum, the addition of acid was injurious, except with butyric acid. The acids tried were formic, acetic, butyric, oxalic, sulphuric, and certain high fatty acids from linseed oil. Carbon dioxide appeared to have no effect. Lewkowitsch (*Analyst.*, 1904 (29), 105) has examined almond, peach-kernel and apricot-kernel oils, and finds that their constants are not a certain means of differentiating between them. The Bieber test (5 parts oil, treated with 1 part of a mixture of sulphuric acid, fuming nitric acid and water) is considered the most useful, but the reagent must be newly prepared, and is not a safe method of detecting adulteration of almond oil with either of the others. He is unable to confirm the statement of Tortelli and Pergami, that most of the fatty acids contain lactonic substances in small amounts. Raikow (*Chem. Ztg.*, 1904 (28), 272) has determined the constants of bear's fat. It is white, similar to lard. It has a lower specific gravity and melting-point than fat from the dog, cat, or fox; the iodine value is rather high. Both the kidney fat and the flare fat were examined, and differ slightly, the former being harder and more opaque. A table of constants is given. Lewkowitsch (*J. Soc. Arts*, 1904 (52)) has printed his Cantor lectures upon the "Uses and Applications of Oils and Fats, and upon the Manufacture of Soap and Candles and Glycerine." Fokin (*Chem. Rev. Fett. u. Harz-Ind.*, 1904 (11)), in a number of articles, reports upon the hydrolysis of fats by the enzyme from castor seeds. There is no difference in the action of the enzymes from different kinds of seeds (wild or cultivated). For maximum hydrolysis, the amount of seeds used is the determining factor and not the quantity of water used. The yield of fatty acids is not much affected by the quantity of water used, if the quantity of seeds be large (20 to 40 per cent.) but with small amounts of seeds (5 per cent.), varying the quantity of water has considerable effect on the yield, owing to the ease with which small amounts of seed separate from the emulsion. The concentration of the glycerol solution depends on the amount of water used in the emulsion and for washing. The glycerol contains albumins, and must be purified. With correct proportions and conditions a yield of 90 to 95 per cent. of fatty acids in three days, is claimed. Thorough mixing and larger amounts of fat used, give higher yields of fatty acids. The acids thus formed are said to be easily bleached. The glycerol solution is not readily separated from the seed residues. The sulphuric or hydrochloric acid used in the emulsion, must not be stronger than N/20, and may be as weak as N/120, with large amounts of seeds. All attempts to get the enzyme in solution failed. Pancreatic juice proved too costly and too slow in its hydrolytic action for technical use. It gave products that were inferior to those from castor seed, and the glycerol had to be separated by "salting out," and is not so pure as that separated from soap-lyes. In the same connection the author has examined

the seeds of about sixty plants and found that more than half of them hydrolyzed fat to the extent of 10 to 16 per cent., but only with the fresh seeds. It is not thought that this is due to an enzyme in all cases, since in two species only, did the yield of fatty acids bear any quantitative relation to the amount of seed used. It is concluded that lipolytic enzymes are not confined to any particular plant family.

HEALTH AND SANITATION.—Renard (*Monit. Scient.*, 1904 (18), 39) reports upon his own suggestion of some years ago, to employ hydrogen peroxide for preserving milk. One or two per cent. of a 12-volume solution, added to milk, decomposes completely in six or eight hours, but larger amounts remain much longer; 5 per cent. added, still showed some undecomposed peroxide after several days. The milk can be kept much longer than untreated milk, without souring. Test samples at 11° C., untreated, soured after twenty-four hours; with 1 per cent. of 12-volume hydrogen peroxide, souring was retarded to eighty hours; with 2 per cent., until ninety hours; and with 3 per cent. after ninety-five hours. A similar test at 20° C., showed souring to occur in much shorter time; *viz.*, after thirteen, twenty-four, twenty-six and thirty-two hours respectively. The peroxide should be added directly after milking, and the milk kept cool for six to eight hours, until the peroxide is decomposed. The odor and taste are said not to be affected, and the milk is claimed to be satisfactory as an infant food. Baker (*J. Soc. Chem. Ind.*, 1904, 159) gives a résumé of the evidence and report of the royal commission on arsenical poisoning, appointed to investigate the epidemic in England, in 1900 and 1902, caused by drinking beer, made from glucose and malt which were contaminated with arsenic. Malt becomes contaminated at times when dried over a fire made with gas-house coke. It was shown that the epidemic in Halifax was characterized by a peripheral neuritis, which alone, could hardly be distinguished from "alcoholic neuritis." It appears that arsenic is usually eliminated from the body with considerable rapidity, but yet it is to be considered "non-cumulative" only in a restricted sense; small doses taken for long periods, result in accumulations in certain tissues; moreover, in the poison cases studied, the signs of arsenical poisoning continued for weeks, after the use of the beer was discontinued. Arsenic was found to be eliminated in the sweat, in the epidermic scales from the skin, in the nails, and especially in the hair. A special study was made of the last, and a large number of analyses made of the hair of patients who had been poisoned, and of others taking arsenic in a medicinal way. In thirty-eight cases where no arsenic had been taken, the hair showed no more than 1/150 grain per pound. Patients who had taken 1/10 grain arsenic daily for two months, showed from 1/20 to 1/5 grain per pound in the hair. The report shows the necessity of excluding even small amounts of arsenic from food and drinks.

A large part of the report deals with the tests and methods of analysis for arsenic in food products. As a rapid and somewhat rough method, the Reinsch test had been employed, but was not to be used for minute traces. The method of generating the hydrogen electrolytically, for converting the arsenic into hydrogen arsenide is recommended when current is available; but the Marsh-Berzelius method, with zinc and hydrochloric acid, is also advocated. The difficulty of getting pure zinc which will not form hydrogen arsenide, is remarked upon. It is stated that quantities of arsenic as small as 0.002 milligram, or 1/720 of a grain, per pound, can be estimated, and smaller quantities detected, to 1/1000 or 1/1300 grain. The destruction of all the organic matter in beer or wort, is advised for the Marsh test; this is not necessary for the electrolytic method. Details of working the apparatus, and the precautions to be taken, are carefully prescribed, together with methods for determining arsenic in coal and fuels. The occurrence of arsenic in yeast, hops, malt, kilned barley, and in anthracite coal and coke used in drying malt, is to be guarded against. A long list of food articles in which arsenic may be present, with a short account in each case of the way it may have been introduced, and the quantities that were found, is included; also the precautions which should be taken by manufacturers to exclude arsenic from their products. A statement of the official control which should be provided by legislation, over the purity of food with reference to arsenic, is given in the report. The net result of the whole investigation is to show that food contamination by arsenic, can usually be traced back to sulphuric acid or to fuel, used at various points in the manufacture. A long discussion by numerous chemists follows the abstract, and throws much light on many of the points raised. Trotman (*J. Soc. Chem. Ind.*, 1904 (177)) describes a modified form of electrolytic method for arsenic-testing (see previous abstract). Seyfferth (*Chem. Centrbl.*, 1904 (1), 472) finds the use of chloroform in cases of inhalation of nitrous fumes, to be very beneficial, when administered in doses of 0.045 to 0.078 gram every ten minutes, until about 0.5 gram has been administered.

Foods.—There has been considerable reference to bleaching methods for flour in the trade papers dealing with milling interests, during the past year or two, and probably there has been some extension of this industry very recently. That any material benefit can accrue to the consumer by these processes seems questionable, and investigations along this line are very desirable. Balland (*Compt. Rend.*, 1904 (139), 822) examined some flour which had been bleached by ozonized air, with a view to determining the changes produced. Although the color was lighter than the untreated flour, the odor had become unpleasant, and there was a noticeable loss of flavor, owing to the fats having become slightly rancid. There was an increase of free acidity from 0.0147 per

cent. in the untreated flour, to 0.0196 per cent., and free fatty acids were extracted with absolute alcohol. Fleurent (*Compt. Rend.*, 1904 (139), 945) states that three methods of bleaching flour, are in use: with ozonized air, with air and nitrogen peroxide, prepared by chemical means, and with air and nitrogen oxides produced by spark discharges. The author holds that the effect of these substances on the fats, acidity, diastase and micro-organisms of the flour, is beneficial, and improve its keeping qualities (see above abstract).

SUGAR.—Gurwitsch (*Ztschr. Ver. deutsch. Zuckerind.*, 1904, 1013) discusses at considerable length the uses of electrolysis in sugar manufacture. He regards electrical methods of purification as more promising for treatment of the molasses than for the original juice or syrup, and at best, only three methods seem promising: (1) the addition of lead saccharate or other basic salt, to the anode; (2) the use of a mercury cathode to take up alkali metals; (3) the use of two diaphragms. He also (*Loc. cit.*, 1045) tried the purification of molasses by diluting largely and electrolyzing, using an iron cathode whose surface is wet with amalgam. The iron anode is partitioned off by a parchment paper septum and a 5 per cent. calcium chloride solution is used in the compartment. The iron in the anode liquor is precipitated by milk of lime, added continually. After electrolysis, the calcium saccharate in the molasses is decomposed with carbon dioxide. Von Lippmann (*Ztschr. Ver. deutsch. Zuckerind.*, 1903 (53), 1131) discusses the losses of sugar in the refinery. He finds that during boiling, a certian amount of sugar is converted into stable bodies, remaining in the syrup, and also into volatile products, such as furfural, acetone, formic and acetic acids, which pass off with the condenser water. Thus in an instance cited, he found 0.75 per cent. of "non-demonstrable" loss, due to chemical changes. Winter (French Patent No. 333813) proposes to make products from beet-sugar which shall have the peculiar flavor of raw cane-sugar, by treating refined beet-sugar with a syrup containing invert sugar and products formed by treating invert sugar with alkalies at fairly high temperatures. Caustic alkalies work best for this, but any alkaline substance can be used. The heating must not be prolonged until caramel is formed.

FERMENTATION, BREWING, ETC.—Van Hest (*Ztschr. ges. Brauw.*, 1903 (26), 614, 701, 787) has published extended investigations upon yeasts. Good top fermentation yeast does not increase the nitrogen content of the wort, but poor yeast does. He found some enzyme action in the case of dead yeast, or where no cell reproduction was noticed, whereby loss of extract in the wort resulted, this being greater than in the case where the yeast remained alive. The zymase present in one liter of yeast cells, is capable of fermenting 870 grams of sugar. The use of sterilized water for washing the yeast is advocated, as the author found the

flocculent yeast sediment carried down most of the bacteria in the water. Excessive washing tends to extract too much of the nitrogenous matter from the yeast. The concentration or number of yeast cells per liter may fluctuate in those cases where top yeast is skimmed off and used for subsequent fermentation, especially if the yeast is washed and allowed to settle after skimming. A formula for the calculation of the quantity of any particular sample of yeast necessary to add to the desired volume of wort, is given, which is based upon a certain standard proportion of yeast of definite number of cells per liter. Seifert (*Ztschr. landw. Vers. Wes. Ost*, 6, 738) has studied a certain "disease" of currant wine, in which turbidity, a decrease of acidity and the acquisition of a harsh taste, were the phenomena noted. Bacteria capable of decomposing the citric acid into acetic acid, water and carbon dioxide, were found in the scum formed; the malic acid also appeared to be converted into lactic acid. The same bacteria are also found in grape wines. The author recommends sulphuring the wine after fermentation, as a protection. Barbier, in a French patent (No. 334071, 1903), proposes to make vinegar from skim milk, by adding sugar, neutralizing the lactic acid with calcium carbonate, and fermenting with yeast to form alcohol. The alcoholic liquid is then infected with the acetic acid ferment, *Mycoderma aceti*, and after acetification is filtered on wood charcoal. Lindner and Matthes (*Ztschr. Spiritusind.*, 1903 (26), 545) describe a disinfectant obtained from by-products of the pottery industry, which they call "montanin." It consists essentially of hydrofluosilicic acid, and is claimed to have no action on the vessels of copper or tin, or on the vat coatings of pitch or lacquer, but it dissolves and disintegrates scale, and prevents growth of micro-organisms and mold. Rayman and Kries (*Woch. Brau.*, 1904 (21), 24) have concluded a series of investigations, begun some years ago, as to the origin of amyl alcohol in fermented liquids. They show that pure cultures of yeast will, under certain circumstances, produce the alcohol, and that bacteria or unhealthy yeast are not the cause. Artificial glucose, fermented with pure yeast, gave no amyl alcohol, but a barley malt decoction yielded it every time. Mixtures of glucose with peptones, when fermented, did not yield the alcohol, nor did beet juice. It is concluded that the carbohydrates accompanying the hexoses were the source of the alcohol. These are supposed to be of the same order as Tollens' "furfuroids," obtained by the hydrolysis of brewers' grains with acids. Windisch (*Woch. Brau.*, 1904 (21), 93), from a study of the cause of albumen or "gluten" turbidity in beer, concludes that it is due to the separation of tin or other metallic compounds of the albuminoids, formed during the filtration of the beer; it is especially noticeable just after the filter has been cleaned, the removal of the beer scale leaving the metal exposed to the beer. Filters with internal enamel, and

horse-hair instead of brass-wire sieves, are recommended. Büchner and Meissenheimer (*Ber. d. chem. Ges.*, 1904 (37), 417) have examined the conditions under which lactic and acetic acids are formed in alcoholic fermentation with the expressed juice of yeast cells. Dêterminations of these acids in the juice, before and after fermentation, showed that the quantity varied in different experiments. In some cases, the lactic acid in the juice disappeared on keeping, and further additions of lactic acid to the juice also disappeared. In other cases, the lactic acid increased. As no sugar was present, it is supposed that the lactic acid was produced from the glycogen. Additions of cane-sugar increased the quantity of lactic acid formed, in most cases. The physiological condition of the yeasts at the time the juice was extracted, is supposed to account for the variations found; zymase probably contains two enzymes, one converting sugar to lactic acid, the other converting lactic acid to alcohol and carbon dioxide. The first is secreted by the lactic acid bacteria, but not the other; but yeast secretes both enzymes. Thus yeast-cell fermentations are of both kinds of enzyme action, and only the final products, alcohol and carbon dioxide, are observed. But with cell juice, as no continuous secretion of enzymes takes place, the final products will depend upon that enzyme which happens to be in excess at the time the extract is made. The authors conclude that lactic acid is only an intermediate product in alcoholic fermentations; glucose is supposed to split into two molecules of lactic acid, which is then hydrolyzed to form ethyl alcohol and carbon dioxide. Acetic acid was formed in the juice on standing for four days, and the amount increased when sugar was added to the juice. Schönfeld (*Woch. Brau.*, 1904 (21), 133) experimented with tin chloride as a cause of turbidity in beer. He found that 0.0005 gram per liter produced much turbidity after twenty-four hours. Strips of aluminum, copper, nickel, brass and antimony, placed in beer, had no effect in seven days, but tin caused turbidity after twenty-four hours, and the action became more marked on longer exposure. Tinned copper and other metals so coated, were more active than pure tin itself, and the conclusion reached is that tinned metals are unsafe to use about any of the brewery fittings. Sellenscheidt (*Woch. Brau.*, 1904 (21), 144) finds that any metal may cause turbidity in beer (see above abstract), but zinc and lead are most active; the marked action of tin is said to be due to lead alloyed with it. Galvanic action is more liable to cause turbidity than direct action of the beer on the metal; aluminum is particularly sensitive to galvanic corrosion. Pure tin is considered the best metal for filter-bodies, as it is less subject to galvanic corrosion; silver plate on brass is too expensive. Soda and other cleansing agents are almost sure to cause turbidity the first time the apparatus is used after their application; after any such cleaning the apparatus

should be left full of stale beer over night, and then washed well with hot water. Low-grade asbestos pulp, used for filters, also causes a turbidity which is very hard to remove. Mohr (*Woch. Brau.*, 1904, (21) 149), from a study of solution of peptone, concludes that the "head" retaining property of beer, bears no relation to its viscosity. The presence of suspended particles of colloid bodies in an exceedingly fine state of division, is assigned as the cause. The agglomeration of these fine particles (causing turbidity) reduces the permanence of the "head." Windisch (*Woch. Brau.*, 1904 (21), 194) adds to the above statement certain instances where filtration has caused noticeable deterioration in the quality of the beer. He also thinks that the removal of the colloid bodies may injure the flavor, as well as reduce the head-retaining property. He asserts that the attempt to get exceedingly clear beers has increased the ratio of metal surfaces and filter exposed to the total volume of the beer. Ludwig agrees with the other writers, but adds that the trouble may be due to the very heavy pressures used in filtering, causing solution of certain impurities in the sludge affecting the taste. Heinzelmann (*Ztschr. Spiritusind.*, 1904 (27), 95) has tested the extractive action of alcohol of various strengths, upon oak wood shavings. The non-volatile matter extracted increased, as the alcohol was more dilute. Previous boiling out of the wood in water, assisted the extraction, by the alcohol. Gelatin, as used to coat the interior of casks, is quite insoluble in 95 per cent. alcohol, but 0.1 gram per liter dissolved in 90 per cent. alcohol, and 0.25 gram per liter in 86 per cent. alcohol. It is not advisable to put crude alcohol of 90 per cent. or less into glued casks. Brand (*Ztschr. ges. Brauw.*, 1904 (27), 115) has examined the action of commercial ammonium fluoride ($NH_4F.HF$) on rubber tubing, as used for disinfecting in breweries. He found that the usual 1 per cent. solutions employed, probably have no injurious action on the rubber, but it may be that badly compounded rubber would show some injury, owing to the action of the acid on the loading materials. Duchemin (*Rev. Gen. de Chim.*, March, 1904) considers a wood distillation product, containing about 65 per cent. methyl alcohol, and having a specific gravity of 0.83, as the best denaturating material for alcohol. About 10 per cent. of this material is used. It does not clog the wicks of the spirit lamps nor give a bad odor when burned, but it has a very disagreeable taste, and cannot be separated from the alcohol. Bonnet has patented in France (No. 339460) certain artificial enzymes, made by adding manganese, iron or copper salts, to albuminous substances, such as gelatine, white of egg, or serum, or to colloids like gum, dextrin, etc., in the presence of a little alkali or alkaline salt, capable of preventing the precipitation of the metallic hydroxide. The material thus formed, acts as a carrier of oxygen, similar to the action of oxidizing enzymes. The material may be sterilized by

heating, or obtained as a solid by precipitation with alcohol, and still retain its oxidizing property. Heinzelmann (*Ztschr. Spiritusind.*, 1904 (27), 399) states that denaturated alcohol of 90 per cent. strength, has more or less solvent action on some metals, especially lead and zinc; iron is less attacked, but in time some oxidation takes place, with some separation of a brown sediment. Copper and brass yield a greenish or bluish color to the liquor, and copper salts remain in the residue after evaporation. Tin seems to withstand all attack, and is recommended as most suitable for this use; tinned iron is especially good, if not abraded. Cement yields a yellow color and lime salts, to the denaturated alcohol. The crude methyl alcohol is supposed to cause most of the corrosion of the metals. Seifert and Reisch (*Ztschr. Spiritusind.*, 1904 (27), 441) find that glycerol is produced in largest quantity during the earlier and most active periods of the alcoholic fermentation of grape must. Glycerol is considered as a metabolic product of the yeast, and the vigor and character of the yeast determines the quantity of glycerol formed. Excess of alcohol tends to retard or stop the formation of glycerol, since it also weakens the yeast growth. Emmerling (*Ber. d. chem. Ges.*, 1904, (37) 3535) finds that very little fusel oil is formed, if all conditions of the alcoholic fermentation are normal, and the wort is pure. Numerous species of bacteria, some of which are found on the skins of the potato, cause the formation of amyl alcohol. Only under anaerobic conditions is the fusel oil formation active. A fermentation of wheat starch and of molasses, when infected with potato skins, yielded much fusel oil, but when converted with malt or inverted with acid, only a trace of fusel oil was produced on fermentation; addition of nitrogenous matter did not increase the production of fusel oil.

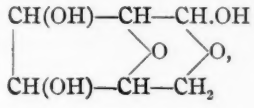
BLEACHING, DYES, ETC.—Fraass (*Farber.-Ztg.*, 1904 (15), 69) considers the cost of electrolytic bleaching by the Schuckert apparatus. Allowing 2000 liters of solution with 2.5 to 2.7 grams available chlorine per liter as required to bleach 500 kilos of goods he finds that a similar amount of liquor can be produced in this apparatus at a cost of 3.88 marks, which he considers a good showing, against the bleach solution made from bleaching-powder. The items of cost are: 29 kilos salt at 0.64 mark; power, 40 amperes at 110 volts, for nine hours, or 39.6 kilowatt hours, at 1.98 marks; depreciation and insurance on plant, at 1.16 marks per day; and sulphuric acid, at 0.10 mark. Breaudat (*Rev. Gen. Mat. Col.*, 1903 (7) 357), in a review of the manufacture of natural indigo in British India, states that bad water is one of the chief obstacles. It is improved by treatment with lime and filtration through sand. He also finds that rapid drying of the indigo affords a product which titrates some 15 to 18 per cent. more indigotine with permanganate, than a slowly dried sample. The author gives no explanation of this, but is of the opinion that neither micro-

organisms nor oxidation by the air, can account for the loss by slow drying. He obtained a black residue of nitrogenous matter, soluble in fuming sulphuric acid, from a low-grade (50 per cent.) indigo, by extracting with water, which he believes is a compound of indigotine, which reduces permanganate. Will and Toeche-Mittler (*Ber. d. chem. Ges.*, 1903 (36), 4390) have published an improved method of making chloranil from *p*-nitraniline, by treatment with potassium chlorate, to form 1,2,6,4,-dichlor-*p*-nitraniline. This is recrystallized from glacial acetic acid, and then reduced by treatment with tin and hydrochloric acid, whereby 2,6-dichlor-*p*-phenylene diamine is formed, which yields chloranil when potassium chlorate is added to the boiling, strongly acid, solution. By recrystallizing from toluene, a product melting at 285°-286° C. is obtained. A yield of 90 per cent. of the theoretical is claimed. Green and Steven have found that formic acid is the best substitute for sulphuric acid, in dyeing mixed cotton and wool goods. It yields faster colors than acetic acid and does not tender the cotton so much as sulphuric acid. The price is not an obstacle. Ehrlich and Sachs (*Ber. d. chem. Ges.*, 1903 (36), 4296) find that by treating an ethereal solution of ethyl bromide with magnesium powder and then adding to the decanted liquid, an ethereal solution of bromo-dimethylaniline, they form dimethyl-aminophenylmagnesium bromide. This, in solution, yields various triphenylmethane dyestuffs, by treatment with Michler's ketone, benzophenone, ethyl benzoate or ethyl naphthonate and similar substances. (Methyl violet, malachite green, etc., are so obtained.) Alliston (*Bull. Soc. Ind., Mulhouse*, 1903 (73), 346) recommends "Hydrosulphite NF" as a means for bleaching the whites of calicoes printed with insoluble azo dyes, where bleaching-powder injures the colors. Hydrosulphite NF is the condensation product of formaldehyde and sodium hydrosulphite; the latter is too easily decomposed for use in this way. Knecht (*Ber. d. chem. Ges.*, 1904 (37), 3479) has determined the quantities of various acid dyes of similar constitution, taken up by wool from baths containing sulphuric acid. He finds that a proportional relation exists between the molecular weight of the dye and the quantity taken up, if the conditions remain unchanged. Large variations in the quantity of dyestuffs used, and of the water in the bath had no material effect on the amount taken up by the fiber. The author discredits the solution theory, and sustains the chemical theory of dyeing. Lob (*Ztschr. Elektrochem.*, 1904 (10), 237) prepares azo dyes electrolytically by passing a current through neutral mixtures of aromatic amines, sodium nitrite and a substance, usually a phenol, to combine with the diazo-compound formed. The mixture is put into the anode compartment and a diaphragm is used. The electrodes must not be attacked. He makes Orange II, from sodium sulphanilate and β-naphthol; Congo red, from benzidine and sodium naphthionate; Chrys-

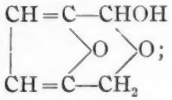
amine G, from benzidine and sodium salicylate, etc.; Dianisidine blue from dianisidine and β-naphthol. Schmidlin (*Compt. Rend.*, 1904 (139), 871), from a study of rosaniline derivatives, considers the cause of coloring properties in dysetuffs, to be the presence of a strongly exothermic group in the molecule, which influences the formation of an endothermic group, containing double bonds, at some other part of the molecule; thus one part of the molecule may be set in vibration by the light waves having a certain wave period. The exothermic groups would correspond to the auxochrome groups of Witt's theory, and the endothermic groups to the chromophores. He supports his theory by citing Helmholtz' hypothesis of absorption, which assumes that a molecule may have central fixed portions and mobile portions, usually in positions of equilibrium with the fixed parts; in cases of absorption, the wave-motion energy is transferred into heat by friction within the molecules, between the fixed and mobile parts. The exothermic and endothermic parts correspond to the fixed and mobile portions assumed by Helmholtz. The Badische Anilin u. Soda Fabrik has taken a French Patent (No. 344680), for making artificial alizarin by heating a mixture of anthraquinone with very concentrated caustic potash-soda solution, and an oxidizing agent, such as sodium chlorate, to 200° C., in open vessels, while stirring thoroughly. The product is extracted with water, and air blown into the solution, while milk of lime is added to precipitate the alizarin. The alizarin is separated from the precipitate, and freed from anthraquinone by treating with hydrochloric acid, and then extracting the residue with dilute caustic soda solution, which dissolves the alizarin.

CELLULOSE.—De Mosenthal (*J. Soc. Chem. Ind.*, 1904, 292) has studied the effect of solvents on cotton and nitrated cotton. His study of the fiber with the microscope, shows the inter-cuticular substance to be made up of minute spherical granules, which lie closely packed and kept in place by the cuticle. He regards the action of cotton upon polarized light as mainly due to tension strains in the layers. The cuticle is stated to contain stomata, and to show distinct porosity when examined under magnification of 1,000 diameters. The stomata lie in oblique rows and appear to lead to lateral channels. The penetration of dyes and mordants into the fiber was ascribed by Walter Crum, to an osmotic action of the cuticle, and the author supports this view. He does not consider capillarity as of much effect in dyeing, his experiments tending to show that it does not take place with single fibers. Nitration produces but little apparent change, but in polarized light it appears that the relative tension of the layers has decreased. The outer cuticle appears more wrinkled. The solvent actions of zinc chloride and ammoniacal cupric oxide are considered to be different; the former destroys the structure, but in the restored cellulose from the latter solution, the intracellular granules

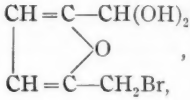
are preserved, and some fragments of the cuticle can be found. Acetone appears to be the only general solvent for nitrated cotton; as a rule, the solubility of the nitrocellulose is not a function of the nitration. The existence of di-, tri-, tetra-, etc., nitrated cotton, is doubted. The viscosity of solutions of nitrated cellulose prepared under different conditions, was found to vary even though the nitrogen percentage was the same in each. Solutions in acetone were evaporated and the granules were seen. A solution of about 1 per cent. can be, to a considerable extent, passed through a Pasteur filter, and if such filtered solution containing granules, is poured into water, the precipitate is a fine powder. A long list of various solvents proposed in patents, is given. In addenda, the author states that he has dialyzed a 5 per cent. solution of nitrated cotton, through a parchment diaphragm. Knecht (*Ber. d. chem. Ges.*, 1904 (37), 549) finds that cotton, nitrated with acid of 1.415 specific gravity, takes a gelatinous appearance, but when washed and dried, the original appearance is restored though a shrinkage of 13 per cent. has occurred. The cotton then shows many of the properties of a mercerized cotton; it has greater affinity for dyes, is stronger, and contains some moisture. By pressing the damp nitrated cotton, to remove the acid, and drying *in vacuo* over lime, the product is unstable, fumes in moist air, and yields nitric acid and cellulose hydrate when digested with water. In dry heat, at 100° C., *in vacuo*, red fumes are set free and a substance is formed, closely resembling oxycellulose. The shrinkage seems to bear some relation to the amount of nitric acid combined with the cellulose, which is also influenced by the strength of acid used. Acid stronger than 1.415 forms ordinary nitrocellulose. The author thinks the unstable body is a cellulose nitrate, $C_6H_{10}O_5$-HNO_3. Flemming (*Chem. Ztg.*, 1904 (28), 213) finds that dichlorhydrin is ten times more powerful than amyl acetate as a solvent for nitrated cellulose, yielding a clear solution. Very concentrated solutions (10 grams in 50 grams solvent), when heated, decomposed somewhat with evolution of nitrous vapors, and the liquid became thinner. He also found that celluloid dissolves in the solvent with some loss of nitrous fumes, this loss diminishing after the solution becomes stronger; very concentrated solutions became solid when benzene, amyl acetate or epichlorhydrin were added; they mix readily with the fatty acids from linseed oil. Green (*Farben. u. Textil-Chem.*, 1904 (3), 97) proposes a formula for cellulose, corresponding to $C_6H_{10}O_5$, and concludes that the fact of cellulose being a colloid, does not imply a high molecular weight. The formula suggested is



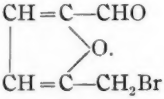
which would be an inner anhydride of glucose. This would explain the formation of glucose from cellulose by hydrolysis. Mercerization probably converts the inner oxygen atoms into —ONa groups, which then yield OH groups. Trinitrate and triacetate derivatives are possible, but tetra-compounds could only be formed after one of the inner oxygen atoms had been replaced by OH. The formation of bromomethylfurfural from cellulose is also explained; thus, by hydration we get



then HBr is absorbed,



which splits out water, leaving



FIBERS AND TEXTILES.—Stocks and White (*J. Soc. Dyers and Colorists*, 1904 (20), 55) have a review of improvements in the sizing of textiles. Cassava root starch is promising as of much use in the future for sizing. By fermentation of flour the albuminoids become largely soluble, sugar is destroyed and free acid is found. This change is most noticeable in two weeks after the flour is prepared; later there is less change. As moulds and bacteria continue to grow the insoluble albuminoids become more noticeable. Fresh flour, if treated with 0.5 per cent. solution of acetic or lactic acid, has its albuminoids made soluble, and acquires the properties of fermented flour. To prevent mould growth a 1 per cent. solution of lactic acid is better than zinc chloride in stronger solution. Loverdo (*Compt. Rend.*, 1904 (138), 1434) proposes to kill the chrysalis of the silkworm by placing the silk-cocoons in chambers kept at temperatures below 0° C. for a month. In this way the cocoons need no particular attention, and no injury results to the fiber, as may easily happen with the hot process.

MERCERIZING.—Hübner and Pope (*J. Soc. Chem. Ind.*, 1904, 404) have continued their studies of the effects of reagents upon the cellulose of the cotton fiber, and have examined the action of mercerizing and other liquids upon the luster, tinctorial properties and structure of cotton. It is shown that cold caustic soda considerably increases the affinity of cotton for direct dyes, and between 0° and 18° Tw., this increase is approximately proportional to the strength of caustic used; from 18° to 22° Tw. there is increase in the affinity developed in proportion to the strength of the caustic, and between 26° and 30° Tw. the most marked increase is found. Between 30° and 65° Tw. the affinity

for the dye is slowly increased, but at 70° Tw. the maximum is reached and stronger solutions cause a marked decrease in the affinity; thus with 80° Tw. the affinity is no stronger than at 35° Tw. Repeating the tests at temperatures of 20° and 80° C. it appears that the affinity decreases with the temperature rise as well as with the concentration. Trials were also made of the action of barium-mercuric oxide, potassium iodide, hydrochloric acid, zinc chloride and nitric acid. The results of the dyeing trials showed that each of these substances causes increase of the affinity for the dye, but with these no reversing effect was found in the high concentrations. The shrinking effect of different concentrations of caustic soda was also examined, and after overcoming numerous difficulties it was found that even 1° Tw. caustic caused noticeably greater shrinkage than did pure water, and there was a uniform increase of shrinkage with the increase of concentration until 20° Tw. was reached, at which strength a sudden increase in the amount of shrinkage occurred. This increases rapidly until a maximum effect was found, at 45° Tw.; above this a decrease of shrinkage took place, but with the solutions above 50° Tw. the viscosity of the liquid is such that in washing, the fiber becomes soaked with a more dilute caustic soda, which itself exerts a more marked shrinking effect. This made it necessary to measure the shrinkage of the yarn without previous washing and while still wet with the lye. The fact has a practical bearing in mercerizing operations; if a liquor of 50° Tw. be used in the machine, the main shrinkage occurs during the impregnation and no additional strain comes on the goods or the machine during washing, but with liquors of 75° or 80° Tw. the greatest shrinkage occurs during the washing out of the caustic, which causes a certain tendency for the goods to tear at that time and which could be avoided by using weaker liquor. The effect on the microscopic appearance and structure of the cotton fiber of the various mercerizing reagents was carefully studied and several photographs are given illustrating these. The authors show that the liquids which cause luster act first to cause swelling and a gelatinous appearance in the fiber, second, a marked tendency to shrinkage, and third, an untwisting of the natural curl of the fiber. The swelling must precede the untwisting to obtain an increased luster. As the ends of the fibers are more or less firmly held the uncurling of a part of the swollen and stretched fiber causes the other portions of the same fiber to twist, perhaps in a reversed direction to each other, hence the appearance of a gelatinous rod, having a series of pieces of cork-screw-like windings, is produced. The original folded ribbon of the raw cotton becomes a straight rod, nearly circular in cross-section and having on its surface, spiral elevations with smooth, rounded edges. These ridges reflect the light from all directions and thus produce the increased luster. An experiment with smooth and twisted

glass rods serves to illustrate the difference between cottons mercerized with and without tension. Beltzer (*Monit. Scient.*, 1904 (18), 732) has reviewed the status of mercerizing as now practiced, dealing with the various operations of preparation, the various liquids used, the several types of apparatus and machines used; dyeing processes and examination of products; also calculations of the cost of the several operations.

PAPER.—Montanus (*Woch. Papierfabrik.*, 1904 (35), 2832) reviews the recent changes in the processes of boiling wood for sulphite pulp. The time of boiling has been cut down more or less, but depends upon the strength of the liquor and the quality of pulp desired; for great strength "high boiling" is customary, the liquor having considerable sulphur dioxide still in solution at the end of the process, but if easily bleached pulp is required "low" boiling, in which nearly all the sulphur dioxide is used, is practiced. Such pulp is brown in color, but bleaches very easily, provided the wood is not scorched. Slow boiling is also essential. The same author (*Loc. cit.*, 2761) also considers the bleaching of sulphite pulp; for full bleach about 14 per cent. of bleaching-powder is needed. No acid is used and the temperature is kept under 40° C. Bleaching is done in the hollander and for pulp that is difficult to decolorize, two treatments with bleaching solution are recommended, but the quantity of bleach used each time is less than would be used ordinarily in the engine. The liquors are used at 3.5° to 4° Bé., but the available chlorine is best determined in each lot.

TANNING, LEATHER.—Eitner (*Der Gerber*, 1904 (30), 173) examined certain specimens of chrome leather containing 5 per cent. of grease, which, on lying in contact with vegetable-tanned leather containing 17 per cent. of grease, showed spueing or white spots at the points of contact. These spots were stearine crystals, which had passed through the chrome leather. It was not proved that they had passed from the vegetable-tanned leather goods to the chrome leather, but considering the colloid nature of the latter it might be possible that the crystallizable stearin has passed through as through a membrane. A case where magnesium sulphate, from the filling of the cloth lining, had passed through and appeared on the surface of boots is mentioned. It is concluded that stearin should not be used in fat-liquor for chrome leather, nor on light calf-skins.

ESSENTIAL OILS.—Heber (English Patent No. 10004, 1903) proposes to deodorize Russian oil of turpentine, petroleum spirit, benzene, etc., by treating with 5 to 10 per cent. of its weight of a 4 per cent. solution of potassium permanganate. Chromic acid and persulphates are also claimed. Treatment with lime, and steam distillation should precede the treatment with the oxidizing agent. Von Soden and Treff (*Ber. d. chem. Ges.*, 1904 (37), 1094) find the alcohol *nerol* present in otto of roses to the extent

of 5 to 10 per cent. There is also about 1 per cent. of eugenol present. By fractionation in vacuum of these alcohols, an alcohol, $C_{15}H_{26}O$, probably identical with the *farnesol* of the oil of acasia flowers, was obtained. This alcohol also is present in otto of roses to about 1 per cent. Power and Lees (*Proc. Chem. Soc.*, 1904 (20), 88) have examined the oil of the California laurel, *Umbellularia Californica*. It has a specific gravity of 0.9483 at 16° C.; in a 100 mm. tube, α_D is —22°; soluble in 1.5 parts of 70 per cent. alcohol. The chief constituents are *umbellulone* (an unsaturated aromatic ketone), $C_{10}H_{14}O$, some 60 per cent.; cineol, 20 per cent.; eugenol methyl ether, 10 per cent.; *l*-pinene, 6 per cent.; eugenol, 1.7 per cent.; and traces of safrol.

India Rubber.—Weber (*India Rubber Jour.*, 1904 (27), 21, 30) points out the possible danger from acid present in the sulphur used for vulcanizing, especially in goods containing no fillers of alkaline nature. Lime ground with sulphur in a ball-mill, is advocated as best for vulcanizing. The same writer, in another article (*Gummi-Ztg.*, 1903 (18), 255), shows that the adhesion between vulcanized rubber and metals, is firmer in proportion to the readiness with which sulphur combines with the metal. Thus copper, lead, silver, arsenic and antimony adhere readily to the rubber; tin, zinc, iron and aluminum less so; and platinum and gold not at all. Thus iron and steel are coated with copper or antimony when firm adhesion of the rubber is desired, while in the case of cables, the copper wire is usually tinned to avoid too tenacious adhesion. Weber (*Gummi-Ztg.*, 1904 (18), 461) notes that the valuation of rubber by the method of fractional precipitation is not safe when used alone on unknown rubbers, and recommends an elementary analysis of the rubber, and also of the fractional precipitates with determinations of the bromine, as a control. An instance in which the method failed to give the true value, is cited. The same author (*India-Rubber Jour.*, 1904 (28), 228) describes the varieties and characteristics of *Castilloa*. The probable returns from its cultivation in Columbia are put at 100 per cent. in the eighth year of growth of the trees. They should not be tapped earlier, since rubber from young trees contains too much resin. An improved process for coagulating the latex without coagulating the albumin, is to dilute it with five volumes of water, strain through cotton gauze, and then add 8 ounces of formaldehyde to each barrel of liquid. After agitation, the liquid is kept quiet for twenty-four hours, when the rubber collects on the surface as a solid, white cake, from which any traces of albumin can easily be washed. Harries (*Ber. d. chem. Ges.*, 1904 (37), 2708) finds that Para rubber dissolved in chloroform is attacked by ozone, and the ozonide formed, decomposes with hot water into keto- and dialdehydes, setting free hydrogen peroxide, which further oxidizes the aldehydes to acids. The ozone compound is obtained as a vitreous mass, after precipitation from its ethyl

acetate solution by adding petroleum spirit. It explodes when heated on platinum foil. The composition corresponds to $(C_{10}H_{16}O_6)_x$, the value of x being uncertain, probably 2 or 3. When thoroughly extracted with water, the extract was chiefly levulinic acid; oxalic acid was not detected, but it is thought to be a product of secondary oxidation of the rubber. Fendler (*Gummi-Ztg.*, 1904 (19), 41) has examined the reaction of solvents on rubber, using some twenty-six varieties in all. He fails to confirm Weber as to the insolubility of rubber in ether, but finds it, on the whole, a fairly good solvent for some varieties. Some rubbers contain substances insoluble in all solvents tried; these are supposed to be oxidation products, or substances formed by the sulphurous acid produced in coagulating the rubber in the smoke of Urikuri nuts. Petroleum spirit extracts the lower oxidation products, while the portions dissolved by benzene contain more oxygen. The author holds that Harries' "nitrosit" method estimates the partially oxidized products as pure rubber, and should be used only for vulcanized rubber.

NEW BOOKS.

AVOGADRO AND DALTON THE STANDING IN CHEMISTRY OF THEIR HYPOTHESES BY ANDREW N. MELDRUM, D.Sc. Edinburgh William F. Clay 1904 Price, 3 shillings.

The chemist has to do with so overwhelming a multitude of facts that sufficient consideration of the principles and assumptions at the basis of the superstructure is not easy. The present interesting essay, whose preparation and printing have been aided by a grant from the Carnegie trustees, will be sure of a welcome. The author's purpose may be stated in his own words: "The theoretical basis of Nernst's system of chemistry is Avogadro's hypothesis. Nernst's book is a comprehensive one, suitable for the student of research. It goes as far as the debatable ground between the known and the unknown. It was doubtless far from Nernst's purpose to expatiate on the rudiments of chemistry. There is reason to believe that it would be of interest, and even of value, to trace the development, in logical order, of the cardinal doctrines of chemistry on the basis of Avogadro's hypothesis."

The first part of the essay contains seven chapters and treats of "the standing in chemistry of Avogadro's hypothesis." The second part, in the same number of chapters, treats of "the standing in chemistry of Dalton's atomic hypothesis." The conclusion of the first part is (1) "that Avogadro's hypothesis may not be regarded as a well established truth," (2) "that Avogadro's

hypothesis being almost universally accepted by chemists has so many fruitful issues that it is the 'very basis and cornerstone' of chemistry." "The chief issues of the hypothesis are: The molecular theory, including the modern theory of solutions, the atomic hypothesis, the doctrine of valency and the periodic system." The conclusion of the second part, if it can be fairly stated by citing a few lines, is as follows: "The idea of atoms was not due to Dalton. What he originated was a persistent attempt to arrive at atomic weights..... The truth is, that in the form which Dalton gave to the atomic theory there never was any certainty about atoms and atomic weights." "Those who maintain that Dalton's conception of the atom is not outworn, but is still with us, have much to answer for."

Of the principles which have led to such a judgment, the essayist says: "In considering scientific doctrine, some definite conception or other of science must be kept in view. In the course of the argument, as a guiding principle or touchstone, I use the dictum that 'science is measurement.'" But this is far from being a definite and true conception of science; it rules out discovery, it excludes the establishment of the development theory from the list of great scientific achievements. This is important in the present case, for there are two questions: (1) Who first discovered what we now believe about the atomic and molecular structure of matter, and (2) who found a method of successfully weighing atoms and molecules? Now Dalton's postulates may be stated as follows: (1) Every element consists of particles which remain undivided in all chemical reactions. (2) All the particles of a given element are equal in weight, but the particles of different elements differ in weight. (3) Every compound consists of particles, all alike and equal in weight, which remain undivided in most physical processes, though divided in some chemical processes, and which are made up of a finite number of the undivided particles of two or more elements. To the particles of the elements he gave the ancient name of atom; to the particles of compounds he gave the name of compound atom; we retain the name atom, but replace the name compound atom with the name molecule.

Whatever we may concede about the first proposition, the second and the third indubitably belong to Dalton, and they are accepted now. To discern them was work of discovery, and

there are many who think discovery not less important than measurement.

The 113 pages of this essay contain some 150 quotations; some are of merely literary interest, like those from Pater or from Cardinal Newman. Most of them are from the original literature of the subject, and show that the essayist has in mind the material required for the formation of independent opinions, and for their defense. Sometimes the style is not quite so clear as the nature of the subject requires, and the frequent study of a single sentence or passage does not escape giving to the whole something which suggests the schoolmen. This kind of study also demands a good deal of skill in interpretation in order to avoid pitfalls, so that many who carefully consider the argument of the essay will often differ from its understanding of opinions. An instance of this is in the assertion that Faraday was an agnostic in regard to the atomic theory, when he himself is quoted as saying that he believed in atoms, but was agnostic in regard to attaching to the atomic theory the notion of little solid particles existing independently of the forces of matter.

It should be said that the essayist is well aware that he is not, at present, on the side with the majority of chemists. The essay is cordially commended as a valuable contribution to the easier understanding of the growth of atomic and molecular conceptions.

EDWARD W. MORLEY.

THE FOLLIES OF SCIENCE AT THE COURT OF RUDOLPH II, 1576–1612. By HENRY CARRINGTON BOLTON. Milwaukee: Pharmaceutical Review Publishing Co. 1904. 8vo., 217 pp. Price, $2.00.

This posthumous volume, by the late H. Carrington Bolton, furnishes an interesting picture of the period when true science was emerging from mediaeval philosophy, and from the snares set in its pathway by the beliefs in magic, witchcraft, alchemy and astrology. In all of these vagaries the Emperor Rudolph was a firm believer, but while he surrounded himself with charlatans of every description, a few real investigators, among them Tycho Brahe and Kepler, were given his help and patronage. Therein the Emperor "builded better than he knew."

To the preparation of this work Dr. Bolton brought all of his remarkable knowledge of early scientific history to bear. The story is told in narrative form and wanders far afield from the Bohemia in which its main scenes are laid. Dr. Dee and his

magic crystal in England; Tycho Brahe at Uraniborg, and other noted and notorious figures march across the stage. There are passages describing the observatories, alchemical laboratories and pharmacies of the sixteenth century, and with them are appropiate full-page illustrations which make the descriptions more real. There are also reproduced recipes for nauseous and complex remedies whereby all diseases may be healed, and directions, couched in alchemical language, for the transmutation of base metals into gold. To any student of the history of science the volume is well worth reading. It occupies a place by itself in scientific literature. F. W. CLARKE.

REFLECTIONS SUGGESTED BY THE NEW THEORY OF MATTER. By the RIGHT HON. ARTHUR JAMES BALFOUR, M.P. New York: Longmans, Green & Co. Paper, 24 pp. Price, 38 cents.

This little pamphlet is a reprint of the presidential address delivered before the British Association for the Advancement of Science at Cambridge, last August. The point of view of the author is largely given in the following quotation. Speaking of the physicist, he says: "He seeks for something deeper than the laws connecting possible objects of experience. His object is physical reality; a reality which may or may not be capable of direct perception; a reality which is in any case independent of it; a reality which constitutes the permanent mechanism of that physical universe with which our immediate empirical connection is so slight and so deceptive." W. A. NOYES.

DIE HETEROGENEN GLEICHGEWICHTE VOM STANDPUNKTE DER PHASENLEHRE. By H. W. BAKHUIS ROOZEBOOM. Zweites Heft: Systeme aus zwei Komponenten. Erster Teil. Braunschweig: Friedrich Vieweg und Sohn. 1904. 14×22 cm.; xii+465 pp. Price, 12.50 marks.

This number deals with two-component systems in which only one liquid phase is possible and in which only the pure components occur as solid phases. To the majority of chemists the methods of determining the solid phases will be one of the interesting chapters. Among these methods the first is the orthodox one of removing the solid phase and analyzing it. This is the one to be employed wherever possible and this is practically the only one used to any extent by inorganic and organic chemists to-day. This method is not applicable for metals, and an examination of the structure under the microscope is the only really reliable way of coming to a correct conclusion. Some conclusions can

also be drawn from a study of the electromotive force of alloys, but this is not a very reliable method. While the author mentions the measurement of conductivity as a means of studying alloys, this method is not at present of the slightest value. Among other methods are the determinations of densities and heats of formation. These last four methods, as well as Tammann's cooling-curve method, are not accurate enough to be of anything more than historical interest.

The section on solubility curves should be of interest to the general chemist, who ought also to read the chapter on polymorphism. While the essential characteristics of monotropic and enantiotropic substances were discussed under one-component systems, the behavior in solutions is, of course, treated in this number.

The author has brought in quantitative and qualitative relations throughout. It remains to be seen whether this is wise. We distinguish sharply between qualitative and quantitative analysis. Since the phase rule is essentially qualitative it seems to the reviewer that the subject can be treated more clearly by the application of the phase rule to qualitative equilibrium followed by the study of quantitative relations classified according to the phase rule. The answer to this, of course, is that no one has ever written a book in which quantitative equilibria were discussed according to the phase-rule classification and that most physical chemists do not know how it should be done.

WILDER D. BANCROFT.

THE ELECTRIC FURNACE. By HENRI MOISSAN, Membre de l'Institut, Professor of Chemistry at the Sorbonne. Translated by A. T. DE MOUILPIED, B.Sc. (Lond.), M.Sc. (Vict.), Ph.D. Assistant Lecturer in Chemistry in the University of Liverpool. London: Edward Arnold. 1904. Octavo, xi+307 pp. Price, $2.75.

This is the second translation of Moissan's "Le Four Électrique", which has appeared in English within a year, each having a preface by the author. The present book contains 13 pages of matter not in Lenher's translation, including descriptions of the carbide of samarium, the silicides of vanadium and cerium, and the borides of silicon. The translator's English is smooth, and the presswork of the book is excellent. Unlike the Lenher translation, it has an index, but it lacks a bibliography. The necessity for a second translation of a work, which could hardly be expected to have more than a limited sale, is, however, not apparent.

JAS. LEWIS HOWE.

TABLES FOR CHEMICAL CALCULATIONS, WITH EXPLANATIONS AND ILLUSTRATIVE EXAMPLES. BY HORACE L. WELLS. New York: Henry Holt & Co. 1903. pp. v+58.

"This little book has been prepared to facilitate chemical calculations by the use of logarithms.. Too often this work is done by the laborious process of simple multiplication and division, in which, to save labor, the use of roughly approximate atomic weights is too prevalent in cases which deserve more accurate treatment."

This extract from the preface indicates the character of the work. It includes, besides a table of five-place logarithms, the usual tables of factors for gravimetric and gas analysis, metallurgical factors and factors for indirect analysis, atomic and formula-weights. The feature of the work is the introduction of its logarithm after each factor and after each formula-weight, thus saving the greater part of the time usually spent in hunting up logarithms. The factors are those most frequently used in inorganic analysis, and no attempt is made to invade the field of proximate organic analysis. All factors have been calculated at least three times independently. The book should prove extremely useful. It is suggested that as it is likely to be used much on the laboratory desk, a future edition might well be bound in a water-proof cover of some material like oil-cloth.

H. N. STOKES.

A SCHEME FOR THE DETECTION OF THE MORE COMMON CLASSES OF CARBON COMPOUNDS. BY FRANK E. WESTON, B.Sc., F.C.S., Lecturer in Chemistry at the Polytechnic, Regent Street. London and New York: Longmans, Green and Co. 1904. pp. viii+56.

The publication of this book is evidence of the fact that teachers of chemistry are beginning to realize that the laboratory training of students of organic chemistry should consist of more than practice in ultimate analysis and in the preparation of organic compounds. A working knowledge of the science requires not only experience in these parts of the subject, but also a facility in identifying unknown compounds by means of their characteristic reactions. It is to help the student in his study of this important part of the subject that this book is written.

A number of sections of the book are devoted to describing the general methods used. An account of the action of the various classes of compounds with such reagents as water, potassium

hydroxide, sulphuric acid, etc., is next given. Then follows a careful description of the tests which should be applied to a substance under investigation after the elements present have been determined. An example will make the author's method clear. A section is devoted to a consideration of the compounds which contain carbon, hydrogen and nitrogen. A list of the classes of compounds falling into this group is first given. Hydrochloric acid serves as a reagent to divide the group into sub-groups. For the compounds insoluble in the reagent special tests are given, which make it possible to identify the class to which the compound studied belongs. A series of tests to be applied to the substances soluble in the acid, follows. These distinguish, for example, primary, secondary and tertiary amines, diamines, hydrazines, alkaloids and pyridine, quinoline and pyrrol and their derivatives. After the class to which the compound belongs has been determined, a study of the physical properties of the substance and of a derivative of it serves to complete the identification of the compound. In the final section is given, in tabular form, the solubilities in water of the different classes of compounds.

While a few general reactions of value in the qualitative examination of organic compounds have been omitted, and while a few of doubtful value have been included, the comprehensive plan has been worked out admirably, and the book is singularly free from errors. JAMES F. NORRIS.

TEN LECTURES ON BIOCHEMISTRY OF MUSCLE AND NERVE. By W. D. HALLIBURTON, M.D., F.R.S. Philadelphia: P. Blakiston's Son & Co. 151 pp.; 33 illustrations. Price, $2.00.

There is, perhaps, no field of physiological chemistry more perplexing to the student or less inviting to the investigator than the chemistry of muscle. In its beginning the subject gave promise, and commanded the attention of several notable investigators, whose results seemed worthy of consideration, but complications soon began to arise, and the questions involved became more obscure the more they were submitted to examination, until the literature has finally fallen into a state of almost hopeless confusion. The appearance of a text-book, therefore, by an active investigator in this field, and one well known for his clearness and power of explanation, will be universally approved; and it may be stated at the beginning, that if the object of a text-book be the development of an idea from the author's point of view,

without considering contradictory evidence, which would tend to confuse the reader, this book is a most decided success.

The sections on muscle pigments, ferments, glycogen, lactic acid, creatinic, phosphocarnic acid, and the chemical changes accompanying contraction, are not different from the treatment of these subjects which may be found in any text-book of physiology, except that this material is subordinated to the sections which follow on muscle clothing and heat rigor. The muscle proteids are considered at length, and the author points out with some justice, that the differences between his own work and the recent work of von Fürth are principally differences in nomenclature alone, the important findings in the two cases being essentially the same. The well-marked stages of heart rigor are shown to occur at temperatures corresponding closely with those at which the muscle proteids coagulate; but the fact that the greatest contraction does not occur at the coagulating temperature of the proteid which exists in greatest amount, is not considered. In reading this argument, which is so clearly presented and so strongly supported, one feels that order has come out of chaos, and is at a loss to understand how so distinguished a physiological chemist as Hammarsten could write in reference to the subject: "The views of the various investigators differ so essentially, that it is difficult to give any correct view of the various notions. . . For these reasons the author is not sure whether he has understood and correctly given the work of the different investigators."

The section on nerve deals largely with matters of histological interest. After a preliminary struggle with the total solids and specific gravity of the brain there follows a very satisfactory treatment of the chemical topography of the nerve-tissue, and the results are detailed of some interesting observations, which the author was able to make with cerebro-spinal fluid discharged from the nose of a patient. The chapter on metabolism of nerve contains nothing of chemical interest, but the treatment of the coagulation of the proteids of nerve which follows, is worthy of as careful a consideration as the corresponding treatment of muscle. The remainder of the book, which deals with chemical changes in nerve during degeneration and regeneration, and also in nervous diseases is a splendid exposition of one of the most readable chapters in physiological chemistry. It is shown that any set of conditions which bring about nerve degeneration, will at the same time

cause the appearance of choline, both in the cerebro-spinal fluid and in the blood, which, of course, means a decomposition of lecithin. Subsequent observers have stated that the crystals which Halliburton believed to be choline platinum chloride were in reality ammonium platinum chloride; but it is difficult to see how this can be true, in view of the confirmatory physiological tests to which Halliburton submitted his material. In every case, the suspected substance was found capable of causing a rise of blood pressure in a normal animal, but not in an animal previously treated with atropine.

Halliburton's book is not a dispassionate treatment of the subject, which takes into account the relative importance of various matters considered, but is rather an expression of an overpowering enthusiasm possessed by the writer for his own work, which often causes trivial matters to assume gigantic importance. This, however, is a defect so rarely found in text-books, that we are more inclined to approve it than condemn it, and have no doubt that the book will be generally read with pleasure.

WALTER JONES.

BACTERIOLOGY AND THE PUBLIC HEALTH. By GEORGE NEWMAN. Philadelphia: P. Blakiston's Son & Co. 1904. 8vo. xx+497 pp. Price, $5.00.

This book is in reality a third edition of "Bacteria, Especially as They Are Related to the Economy of Nature, to Industrial Processes, and to the Public Health," issued in 1899, in the Science Series, published by Putnam's Sons. In its present form, however, it purports to be a new book, since several new chapters have been added, and the whole enlarged and revised.

The first chapter on the Biology of Bacteria is very short compared with the rest of the book, comprising less than 30 pages. In this there are a number of statements of doubtful accuracy, while others are ambiguous or misleading, *e.g.*, the word capsule is used to designate the cell wall; the modes of reproduction are described as budding, division, and spore-formation for the bacteria and yeasts, but it is not definitely stated which method characterizes each class; chemiotaxis, without further comment, is described as "the somewhat mysterious power by which cells possess inherent attraction or repulsion for other cells;" whereas, it is a response to chemical stimuli, and oxygen and the potassium salts are among the most powerful chemiotactic agents. In this

chapter, also, a half page only is devoted to the bacterial plant diseases, and while such diseases are recognized, no mention is made of several well-known diseases where the etiology has been well worked out, as for instance, pear blight and cabbage rot.

The author's discussion of the subjects of bacteria in their relation to water, to air, to soil, to sewage, to milk and other food supplies, and to the various fermentations, is especially good. Here in 250 pages (Chapters II to VIII inclusive) is given an excellent digest of our present knowledge of these subjects. The general reader, as well as the chemist, biologist, hygienist and medical man, will find these chapters both interesting and instructive. The frequent foot-note references here, as throughout the volume, add much to its value.

The chapters on the relation of bacteria to disease production occupy 170 pages. One describes how bacteria produce disease, channels of infection, etc., and then takes up in outline some of the most important human diseases. Another chapter considers tuberculosis as a type of bacterial disease. This is a good digest of the subject, and contains quite a full discussion of the question of the intercommunicability of the human and bovine types. A third chapter considers the etiology of tropical diseases.

The two final chapters treat of the question of immunity and antitoxins and of disinfection.

It is unfortunate that the addition of the new matter, about 150 pages, and the new dress of the book, should have raised the price from $2.00, that of the first edition, to $5.00, the price of the present one. This has been necessitated, in part at least, by the introduction of a large number of full-page plates, 31 in all. While these plates are of average merit they do not seem to the reviewer to be necessary or even desirable in a work of this general nature. Quite as much value would be gotten from good line drawings in the text. There are three colored plates of the acid-fast bacteria. These are of questionable value in any book, and seem entirely out of place here.

On the whole, however, the book is an excellent one. The literary style is good, and the author has succeeded in presenting the important facts relating to our present knowledge of the bacteria in a simple, attractive, and in general, an accurate way. The publishers have done their part well, and it is to be hoped that in its new form the book will reach a wide circle of readers and students.

W. D. FROST.

CHEMISCH TECHNISCHE UNTERSUCHUNGS METHODEN. VON DR. GEORG LUNGE. Zweiter Band mit 150 Abbildungen, Funfte Auflage. Berlin: Julius Springer. 8vo. xx+842 pp. Price, 16 marks; bound, 18 marks.

The fourth edition was printed in 1900, which shows that the book is in demand. The part treating of iron, by Th. Beckert, comprises 104 pages. The process for the determination of silicon in iron with nitric and sulphuric acids is ascribed in this, as in the fourth edition, to Brown. It should read Drown. No reference is made to the numerous forms of platinum apparatus, of which Shimer's was the first, for burning the carbon in air or oxygen. The combustion of the separated carbon in oxygen takes up just about one-fourth page—far too little space for satisfactory treatment. Knorre's method of precipitating manganese as dioxide by ammonium persulphate is given, but the colorimetric process, founded upon the conversion into permanganate in a nitric acid solution in presence of silver nitrate, is not mentioned. The number of pages devoted to iron (104) is the same in both editions. The section on "Metals Other Than Iron," by Dr. O. Pufahl, comprises 276 pages. Under silver no mention is made of the use of cement cupels. Under the electrolytic determination of copper no reference is made to the use of rotating electrodes. The examination of artificial manures, by Dr. O. Böttcher, takes up 67 pages, 25 pages are devoted to fodders, edited by Dr. F. Barnstein; 44 to explosives, edited by O. Guttmann; 30 pages to fireworks, edited by Wladimir Jettel; 161 pages to gas and ammonia, by Drs. Otto Pfeiffer and G. Lunge; 19 pages to calcium carbide and acetylene, by Dr. G. Lunge; 72 pages to coal tar, by Dr. H. Köhler; and 46 pages to the inorganic colors, by Dr. R. Gnehm.

In a work of such magnitude, contributed to by so many persons, some unevenness of treatment, and some errors both of omission and commission are to be expected, but the book, like preceding editions, is well written and carefully edited.

EDWARD HART.

CHEMISCHE TECHNOLOGIE UND ANALYZE DER OELE FETTE UND WACHSE, VON DR. J. LEWKOWITSCH. Zwei Bande, Band I, 448, Bd. II, 768 Seiten. Braunschweig: Friedr. Vieweg und Sohn. Preis geheftet, 32, gebunden, 34 Marks.

This work appeared originally as a translation and enlargement of Benedikt "Die Analyse der Fette und Wachsarten," and now after passing through two English editions, expanding each time, reappears in a German edition from the third English. When it

came out in 1895, it was immediately recognized as the best book in its field—particularly on the analytical side; this proud distinction it has maintained for ten years, and has now added to it the technical side.

The work is exhaustive, encyclopedic—as nearly complete, perhaps, as it is possible for one person to make it; only those methods are described which have been shown to be practically valuable, most of them having been tried by the author and his assistants—and in many cases the rich experience of twenty years is brought to bear in suggesting opportunities for improvements in these processes and their criticism. It contains further numerous original investigations which have not been previously published.

While the constants of the animal and vegetable oils are so complete, the reviewer feels that it would have added to the value of the treatise had a few pages been devoted to such constants as are available for the petroleum products, as specific gravity, flash test, fire test, viscosity, and cold test; it would have been of advantage furthermore, to have had a statement of what these constants should be, or what are usually considered admissible, for oils for various purposes, as a spindle oil, engine oil, gas engine cylinder oil, etc. This would oftentimes enable the oil chemist to settle vexed questions dealing with lubricating oils with the same authority as in the case of fatty oils—olive oil, for example.

No mention is made of turpentine oil, that being possibly considered as a volatile or essential oil, and not expected to be discussed here; as supplementing the work on linseed oil and varnishes its inclusion would certainly have seemed appropriate, and would have been very convenient. No extended notice is paid to rosin oils, which find considerable use in this country.

On the other hand, no fatty oil is omitted—one finds goose grease and rattlesnake oil, as well as the rare fats from India and Africa; the waste fats, too, receive particular attention, as is given in no other work—some twenty pages being devoted to them.

A noticeable feature of the book is the polyglot nature of the numerous references to the literature of the subject, which is not usual, particularly with books published in the German language. Italian, French, English, American and German periodicals are quoted.

The typography and illustrations are executed with the care and skill for which the house of Vieweg is noted.

A. H. GILL.

TECHNO-CHEMICAL ANALYSIS. BY DR. G. LUNGE. Authorized Translation by ALFRED I. COHN. New York: John Wiley & Sons. 1905. 136 pp. Price, $1.00.

This little book is perhaps best described as an extended index to Lunge's "Chemische-Technische Untersuchungsmethoden." It deals in a general way with all the analytical methods involved in chemical manufactures. In its small compass it is not to be expected that other than the more important methods could be described in detail, and such is the case. Nearly one-third of the volume is devoted to gas analysis and the measurement of gases, perhaps because this branch of volumetric analysis is coming to be more extensively employed in technical work.

In some cases the translator has followed the German idioms too closely; this is seen in carbonic-acid-free-lyes, pyrogallol-potassium, steam cylinder oils, araeometer, a gas burette enclosed in a water mantle, and Stassfurter potassium chloride.

The work will, doubtless, be found valuable to those wishing a general view of the field of analytical chemistry as applied to the industries of the Continent, no reference being made to English or American literature. A. H. GILL.

METHODS OF ANALYSIS OF THE CENTRAL LABORATORY OF THE ITALIAN CUSTOMS HOUSE. BY DR. VITTORIO VILLAVECHIA, Director. Rome: P. Scott & Co. 1904.

Volume V of the report of the Central Laboratory of the Italian Customs Service is published in two parts. Part First, 602 pages, is devoted to a description of the methods used for the examination of water, chemical products, fertilizers, cementing materials, combustibles, coal tar and its products, mineral oils and products derived therefrom, fatty substances, artificial industrial products coming from fats, and milk and its products.

The second volume, 663 pages, treats of essential oils, turpentine and its products, starches and derivative products, sugar and substances containing sugar, spirits and liquors, beers, wines, coloring-materials, varnishes, and textile fabrics.

In the year 1903, 11,668 samples were examined in the Customs Laboratory. Of these sugars represented 6,230; beers, 1,653; mineral oils, 1,253; wines and vermouth, 674; fats, soaps and

waxes, 502; textile fabrics, 723; and candies, fruits and syrups, 406. This work the director of the laboratory undertook, in collaboration with his assistants in the Central Laboratory, Drs. Fabris and Rossi.

In many cases the official methods practiced by the Customs House are the same as those used by the chemists of the agricultural stations, and also coincide with those which have been presented by the International Congress of Applied Chemistry. Special methods, which have originated in the Central Laboratory, are given in great detail, and are submitted now for the first time to general scrutiny.

After each of the main subjects, there is appended a bibliography of the authors cited and the methods described. It is a rather remarkable fact, however, that among the official methods which have been adopted by the Italian Customs Service, as applied to agricultural products, no reference has been made whatever to the work of the Official Agricultural Chemists of this country. While the work contains references to individual investigators in this country, the official methods are not mentioned.

This work will be useful to those engaged in customs work, and especially to those interested in products which are to be imported from or sent to Italy, particularly in those products which must undergo examination before being admitted into that country.

H. W. WILEY.

ANALYSIS OF POTABLE SPIRITS. By S. ARCHIBALD VASEY. London: Bailliere, Tindall & Cox. 1904. Price, 3 shillings.

This little book of 87 pages gives a resumé of the proposed methods for examining potable spirits. It is particularly intended for the guide of analysts in the examination of whisky, brandy, gin and rum. The art of manufacturing imitation whisky, known in this country as compounded or blended whisky, is evidently as far advanced in Great Britain as in the United States.

In regard to these artificial whiskies the author says: "The introduction of grain or neutral spirit was never demanded by public taste; it was dictated solely and simply by economical motives. The time required for maturing genuine whisky is thus saved, and the practice of blending is carried to an enormous, if not appalling, extent, with handsome profits to the blenders."

The author describes the chemical analysis of potable spirits and, briefly, the methods of preparation. He also calls attention to

the fact that the pot-still, that is a still without rectifying column, is the only one which can furnish the raw material which by proper aging becomes potable spirits. Scotch whisky is defined as being a pure malt whisky.

Chapter III treats of the standards used in analysis, most of the processes being of a colorimetric nature, especially in the determination of small quantities of materials found in both distilled malt spirits and in brandies.

The fourth chapter is devoted to the estimation of aldehydes and acids. The aldehydes are taken as existing in the form of acetaldehyde CH_3COH. In the colorimetric method of determining aldehyde the free aldehyde is prepared from the ammonia aldehyde $CH_3CHOHNH_2$.

Chapter V is devoted to the estimation of higher alcohols commonly grouped together under the term "fusel oil." The principal higher alcohols are propyl, normal butyl, isobutyl and amyl. The percentage of these bodies in fusel oil varies greatly, but normal butyl alcohol and amyl alcohol constitute the chief portions thereof.

The process of determining the higher alcohols consists in oxidizing them to the corresponding acids, and throwing these out as barium salt. Carbon tetrachloride is recommended instead of chloroform for dissolving the higher alcohols because carbon tetrachloride yields no mineral acid on oxidation with chromic acid.

The colorimetric methods, especially those of Girard and Cuniasse, are fully described, but these are more valuable as qualitative than quantitative processes.

The sixth chapter is devoted to the estimation of compound ethers, and the seventh to the estimation of furfural.

Chapter VIII describes the importance of taste in judging between genuine and imitation distilled potable spirits, and Chapter IX is given up to general considerations of the results of analysis.

The author is of the opinion that generally by the sense of taste and the results of analysis the genuine pot-distilled potable spirits can be distinguished from those compounded with neutral spirits, and artificial essences.

It must be admitted, however, that the skilled chemist might so compound these bodies as to make the analytical data very dif-

ficult of interpretation. In such cases the educated taste would be of great help.

The final chapter is given to descriptions of different colorimeters which are used.

This little work will be a great help to analysts, who do not have the larger works referred to by the author, and even those who have them at hand would find this compilation time saving. It is evident that much light may be thrown upon the composition of potable spirits by careful chemical investigations. Fortunately, however, in all civilized countries potable spirits are subjected to the strictest fiscal regulations, and by reason of this supervision it should not be difficult in any case to trace a sample to its origin, and to determine by the inspection of the public records whether it is a pure, straight pot-distilled liquor, or an imitation article made from neutral spirits, artificially colored and containing such substances as the compounder may see fit to use.

H. W. WILEY.

ELECTRICITY IN AGRICULTURE AND HORTICULTURE. By PROF. S. LEMSTROM. New York: D. Van Nostrand Co. Price, $1.50.

This book of 72 pages is devoted to a description of experiments in the application of electricity to agriculture and horticulture. The author conducted his original experiments with the old electrical machines of Holtz, and gives a number of data showing the effect of electrical influences upon vegetation. The object was not to produce an electric light in order that the period of work of the chlorophyll cells might be lengthened, but to subject the plants and the soil to the emanations of the ordinary Holtz electrical machine. The author has constructed a special electrical apparatus which is described in detail, to take the place of the Holtz machine. The experimental part is followed by a discussion of the question, "How does electricity exercise its influence on the plants?" The author draws the following conclusions: "The electric current produced by the influence machine when its positive pole is earthed goes from the earth through the plants to the points of the insulated wire-net, and back to the negative pole. This causes an ascent of liquid or juice in the capillary tubes of the plants, and produces in such a way an augmentation of the energy with which the circulation of the juices is going on."

It is hardly to be expected that the data and methods described

should be seriously regarded as any real, practical aid to agriculture. The connection between the electrical influence exercised and the growth of the plant is surely not demonstrated to such an extent as to warrant the conclusion above drawn. There is one conclusion of the author, however, with which we all most heartily agree, namely: "The better and more scientifically a field is cultivated and manured, the greater is the increased per cent. On poor soil it is so small as to be scarcely perceptible."

This little book will prove interesting to experimenters along agricultural lines, and I am far from desiring to say that there is not much in it which is valuable. Its suggestions are at least worthy of respectful consideration. H. W. WILEY.

CORRECTION.

The price of the "Phase Rule," by Alexander Findlay, is $1.60 instead of $1.25 as given in the Review in the March number of this Journal.